SOLID-STATE REACTION BETWEEN TWO OXIDES.

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DECLARATION

I asseverate that this is completely my own work unless otherwise stated.

Signed, Brian Cormack.

I further declare that I attended the following post-graduate lectures, seminars or courses:-

" Colloids and Money" - Dr B A Pethica and Dr P Anderson (Unilever Research).

" Chemical aspects of Molecular Biology" - Dr R P Ambler.

" Specialist N.M.R. course" - Dr P M Lyndon-Bell.

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ABSTRACT

Reactions between solid oxides were studied for the systems Ln_2O_3-Cr_2O_3; Ln = La, Pr and Y, by following the variation of products with temperature or time, at temperatures below 1000°C, employing predominantly chemical analysis.

In the La_2O_3-Cr_2O_3 system three products formed in an atmosphere of air or oxygen, $LaCrO_4$, $La_2(CrO_4)_3$ and $LaCrO_3$. The chromate (V) compound decomposes to chromite at temperatures around 600°C, whereas the chromate (VI) compound decomposes at slightly higher temperatures. In argon only $LaCrO_3$ formed. The way in which the two chromates are formed, and decompose to chromite was delineated and a mechanism was advanced in explanation.

The only significant product in the Y_2O_3-Cr_2O_3 system, $YCrO_3$, formed in varying extent in different atmospheres in the order argon $\ll$ air $<$ oxygen. The experimental evidence was related to a mechanism for chromite formation.

The Pr_2O_3-Cr_2O_3 system was complicated, by the oxidation of the Pr_2O_3 oxide, in air or oxygen atmosphere. The variation in the oxidation state of the oxide was followed analytically during the reaction, thus affording a more precise investigation of the nature of its interaction with chromic oxide. A mechanism for chromate (VI) formation and decomposition to the chromite, was propounded. In this system $PrCrO_4$ formed in an isothermal at 560°C.

CONTENTS

INTRODUCTION

A study of the kinetics and mechanism of the solid-solid interaction between chromium (III) oxide and the lanthanide (III) oxides of yttrium, praseodymium, and lanthanum, at temperatures below 1000°C with the phases identified by chemical analysis forms the substance of this work. This is an extension of the examination of the Nd_2O_3-Cr_2O_3 system, previously undertaken (Gibb, 1973).

There was no intention to study methods of synthesis, or prepare 100% purity of any phase, but the possible products of reactions in the lanthanide (III) oxide - chromic oxide systems which have been prepared and had, in many cases, their structure determined are the chromates (VI) and (V) and the chromites. It is of interest, therefore, to describe briefly when and under what conditions these compounds and their structures have been reported.

The first reported synthesis of any chromate of the lanthanides was the preparation of $Ln_2(CrO_4)_3.8H_2O$, Ln = La, Pr, Nd, Sm (Britton, 1925) from solution. That same year the anhydrous chromates (VI) were prepared, all except the cerium compound by the dehydration of the precipitated hydrated compound (Zambanini and Carobbi, 1925).

The preparation of the chromates (VI) of the lanthanides $Ln_2(CrO_4)_3.8H_2O$ was also achieved by Schwarz (1963) using in all cases an aqueous lanthanum nitrate solution and with, either, a stoichiometric solution of chromium trioxide, from which the product

was precipitated by the addition of NaOH dropwise, Ln = La, or by adding a 10% excess solution of sodium chromate Ln = Nd, Sm, Pr. The anhydrous product was obtained by heating the hydrated compound for approximately 2h at 400°C. The preparation of $Pr_2(CrO_4)_3.8H_2O$ was also reported using a method similar to that of Schwarz for Ln = La, (Perel'man and Fedoseeva, 1963). The analogous yttrium compounds have not been prepared, although the compound of formula $Y(OH)Cr^{VI}O_4(Y_2O_3\text{-}2CrO_3.1.08H_2O)$ does exist (Schwarz, 1963). There is no solid state preparation of the chromates (VI) detailed in the literature.

The structures of the lanthanide chromates (VI) have not been ascertained, although it was stated (Darrie, 1967) that the structures might be similar to that of $MgCrO_4$ with chains of chromate (VI) tetrahedra. In an infra-red study of the hydrated chromates (VI), (Petrov et al, 1975), a structure containing isolated tetrahedra was postulated.

The preparation of the lanthanide chromates (VI) (Schwarz, 1963) was achieved using a variety of methods represented by the equations below:-

1) $2Ln_2(CrO_4)_3.aq. + Ln_2O_3.aq \rightarrow 6LnCrO_4 + 1\frac{1}{2}O_2 + aq.$

2) $Ln_2(CrO_4)_3 + Ln(NO_3)_3.6H_2O \rightarrow 3LnCrO_4 + 3NO_2 + 1\frac{1}{2}O_2$

3) $Cr(NO_3)_3.9H_2O + Ln(NO_3)_3.6H_2O \rightarrow LnCrO_4 + NO_2 + 1\frac{1}{2}O_2$

4) $Cr_2O_3aq. + Ln_2O_3aq. + O_2 \rightarrow LnCrO_4 + aq.$

The mixtures were heated in an atmosphere of oxygen at

temperatures below 650°C. Not every method was found suitable for every lanthanide; reaction 2) was preferred for praseodymium, and the decomposition of Y_2O_3-$2CrO_3$. $1.08H_2O$ for formation of $YCrO_4$; although Pryde (1971) applied method 3) to a wide range of lanthanides including praseodymium and yttrium. This method was also used successfully by Bertaut et al (1964) for the preparation of lanthanum chromates (V) of Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, La and Y.

The method favoured for the preparation of $YCrO_4$ by Schwarz, 1963 was the decomposition of the $Y(OH)Cr^{VI}O_4$ compound. It was also stated by him, on the basis of evidence from thermogravimetry, that for Ln = La, Nd, the chromate (V) was produced as an unstable intermediate in the decomposition of the anhydrous chromates (VI). This was confirmed by Kirkpatrick (1966) for neodymium; Darrie (1967); and Pryde (1971) for praseodymium, but this was not a suitable method of preparation. The equations given are:-

1. $$Ln_2(CrO_4)_3 \rightarrow 2LnCrO_4 + 0.5\,Cr_2O_3 + 1.25O_2$$

2. $$2LnCrO_4 \rightarrow 2LnCrO_3 .$$

Neodymium chromate (V) was also obtained (Gibb, 1973) from the solid-solid interaction of the anhydrous chromate (V), prepared from solution, and the requisite amount of neodymium oxide, according to the equation:-

$$Nd_2(CrO_4)_3 + \tfrac{1}{2}\,Nd_2O_3 \rightarrow NdCrO_4.$$

Under the appropriate conditions of temperature, 525°C, and time 7Oh, 1OO°/o yield was obtained.

The lanthanide chromates (V) have the tetragonal zircon structure [Schwarz (1963); Bertaut et al. (1964)]; with the exception of lanthanum chromate (V), which has the monoclinic huttonite structure (Schwarz, 1963); and praseodymium chromate (V), which has been shown to have a mixture of huttonite and zircon structures [Schwarz (1963) ; Pryde (1971)].

Since the mid 195O's numerous solid state preparations of the lanthanides chromites have been described. The chromites $LnCrO_3$, Ln = La, Ce, Pr, Nd were first synthesised (Wold and Ward, 1954) by heating intimate mixtures of chromium (III) oxide and the lanthanide (III) oxides in air at 9OO°C. About the same time $YCrO_3$ was prepared by reaction of Cr_2O_3 and Y_2O_3 in a NaCl flux at 9OO°C under a hydrogen atmosphere (Looby and Katz, 1954). A wide range of chromites were also synthesised (Ruggiera and Ferro, 1955) by heating a compact of the two oxides at 135O°C for 3Omin., and then at 1OOO°C for 3O - 4Ohours; but it is noteworthy in view of the paucity of information on the reactions of Pr_2O_3 or P_6O_{11} with Cr_2O_3 that the reaction of Pr_6O_{11} with Cr_2O_3 occurred in a few minutes with evolution of oxygen. A similar general method of preparation has been used by Schneider et al. (1961).

The chromite can also be formed by decomposition of a mixture of the nitrates (Portnoi and Timofeeva, 1965) at 11OO-12OO°K

or by decomposition of the chromates (VI) or chromates (V) (Schwarz, 1963) above 650°C.

The structures of the chromites were variously reported as being ideal cubic perovskite (Ruggiero and Ferro, 1955) or with a slight modification of this structure (Schneider et al. 1961). It may be, that apart from $LaCrO_3$ which appears to have the ideal perovskite structure (Darrie, 1967), that all other lanthanide chromites have an orthorhombic modification, with the degree of distortion increasing from La to Lu (Quezel-Ambrunaz and Mareschal, 1963).

In the study of the systems Ln_2O_3-Cr_2O_3 there was an initial, almost exclusive, concentration on high temperature studies above 1000°C, for the construction of phase diagrams. For this purpose the majority of the lanthanide (III) oxide systems were studied. The results can be succintly stated: in each case only one product was formed, the chromite , $LnCrO_3$, which has the perovskite structure. The systems studied were Ln = La, Nd (Andreeva and Keler, 1966), Ln = Ce (Leonov, 1966) and (Koehler, 1971), Ln = Sm (Lopato, 1966), Ln = Dy (Shevchenko and Lopato, 1969), Ln = Eu (Shevchenko and Lopato, 1967), Ln = La (Cassedanne, 1968), Ln = La (Pavlikov and Tresvyatskii, 1964), Ln = Nd (Pavlikov and Tresvyatskii, 1966) and Ln = Pr, Sm, Y (Pavlikov et al., 1966).

Despite an increase in the availability of literature from the mid-1960's onward on the kinetics and mechanism of the

interaction between lanthanide (III) oxides and chromic oxide the amount of information available is still relatively small. Therefore this survey has been extended to include the lanthanide (III) salts and hydroxides, usually reacted with chromic oxide or chromium (III) hydroxide.

Two main approaches are evident in the study of kinetics and mechanism in these systems:

1) A complete chemical analysis of all the possible products together with the starting oxides, supplemented with physical data. This was first used by Gibb (1973) and allows an extremely thorough examination of these systems.

2) The Russian approach. This places the major emphasis on the physical techniques, infra-red spectroscopy, x-ray diffractometry , and ultra-violet diffuse reflectance spectroscopy. In addition, various methods of chemical analysis were used, but primarily the dissolution of unreacted rare earth oxide to follow the course of the reaction.

It is important to examine closely the work done on these systems; and in detail, the techniques involved and the conclusions drawn.

The first report of a soluble chromate forming from the reaction of a lanthanide (III) oxide and chromic oxide occurred in a study of the La_2O_3-Cr_2O_3 system in air (Tresvyatskii and Pavlikov, 1964) for the construction of a phase diagram. They state that

$La_2(CrO_4)_3$ was present at temperatures below 1000°C; while, above this temperature and in argon chromite was the only product.

In an examination of the systems Sm_2O_3-Cr_2O_3 and Eu_2O_3-Cr_2O_3 (Portnoi, 1965) both x-ray powder diffraction analysis and chemical analysis were employed. The rare earth oxides were both of 99.9% purity, with the chromic oxide used of 98.7% purity. Mixtures were prepared in several molar ratios, with Sm_2O_3 in excess, Cr_2O_3 in excess, and in a ratio of 1:1. After reaction the mixture was boiled in 50% hydrochloric acid for 1h to dissolve any remaining rare earth oxide. The remaining residue was then subject to x-ray and chemical analysis, but Cr_2O_3 and $LnCrO_3$ were unable to be separated. In the Sm_2O_3-Cr_2O_3 system this residue contained $SmCrO_3/Cr_2O_3$, with chromic oxide in excess, in the original mixture, when reacted at temperatures above 800°C for 5h; whereas mixtures with ratios of 1:1 or with Sm_2O_3 in excess contained only $SmCrO_3$. Thus the reaction goes to completion above 800°C. Formation of 6.2% chromite was reported after 2h reaction at 400°C, and at 660°C after 2h reaction, the yield of chromite was 49.1%.

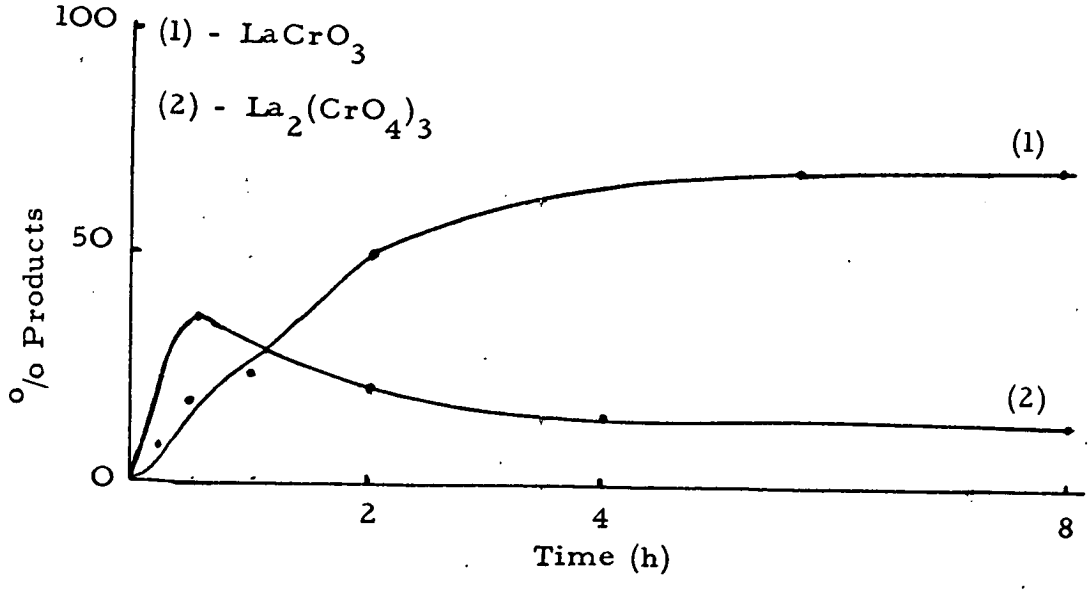
Similar results were obtained in the Eu_2O_3-Cr_2O_3 system, there was only one product $EuCrO_3$.

The systems La_2O_3-Cr_2O_3 and Y_2O_3-Cr_2O_3 were investigated (Rubinchik et al., 1969) in order to study the conditions of temperature required for the formation of $LaCrO_3$ and $YCrO_3$ and to elucidate the kinetics and mechanism of this reaction. Starting

oxides of at least 99°/o purity were used to prepare a mixture for reaction in a stoichiometric ratio of 1:1, which was then pressed to form pellets. The chemical analysis used a 30°/o solution of ammonium acetate maintained at 80°C for 70 min. to dissolve out free lanthanide (III) oxide. This 'free oxide' was then determined by titration. Further information on phase changes was obtained from x-ray powder diffraction analysis data and infra-red spectroscopy using KBr discs.

In the La_2O_3-Cr_2O_3 system it is reported that reaction began in the range 350-400°C. This was shown by 1) a change in weight, 2) a colour change to a yellowish green shade which remained when dissolved in ammonium acetate. These changes were ascribed to oxidation of chromium (III) to chromium (VI). By these means the presence of chromate to 800°C was reported.

The reaction kinetics in an isothermal at 600°C, in the period 0-8h is shown in the diagram below.



The most significant features are a maximum in chromate formation after 30 min. with a rapid decrease in the period up to 4h, and an initial low yield of chromite, whose rate of formation increases with time from 0-2h.

The decrease in the amount of chromate (VI) was explained as rate of decrease greater than rate of increase as the reaction proceeds with formation of chromite and depletion of starting oxides. Thus, it was concluded that formation of chromite occurs through intermediate products. The reactions for the formation of chromite were given as follows:-

$$2La_2O_3 + 3Cr_2O_3 + 9/2O_2 \rightarrow 2La_2(CrO_4)_3 \quad (1)$$

$$2La_2(CrO_4)_3 \rightarrow 4LaCrO_3 + Cr_2O_3 + {}^{9}/_{2}O_2 \quad (2)$$

There was also infra-red evidence for the presence of $La_2(CrO_4)_3$ between 500 and 700°C. Three narrow bands in the region 900-1000 cm^{-1} were ascribed to lanthanum chromate (VI) in concordance with those of Darrie, 1967.

To test the mechanism involving oxidised intermediates the reaction $La_2O_3 + Cr_2O_3$ was studied in a controlled oxygen atmosphere. At 600°C it was found that the partial pressure of oxygen decreased for the initial 4h of reaction and increased from 4 to 6.1/2h as, presumably, the rate of decomposition of chromate exceeded the rate of formation.

The reaction was also studied isothermally at 900°C in argon, where formation of chromite was considerably slower than in

air.

The system Y_2O_3-Cr_2O_3 showed many differences. Reaction began at 600°C but no chromate was detected and although the absence of starting oxides from x-ray work was observed in the La_2O_3-Cr_2O_3 system at 1150°C, this was not so until 1400°C in the Y_2O_3-Cr_2O_3 system.

That the rate of formation of chromite in this system was much slower than that in the lanthanum system was shown by the detection of unreacted oxide in isothermals in air at 750, 800 and 850°C. Kinetic data were fitted with equations since no intermediate compounds were formed.

In a subsequent examination of the effect of a gaseous medium on the kinetics and mechanism of lanthanum chromite formation (Rubinichik et al., 1972), the system was studied in an oxygen atmosphere between 1-740 torr., in vacuo at 2×10^{-2} torr., and with water vapour present from 1-15 torr. To follow the course of the reaction, the techniques of x-ray powder diffractometry, infra-red spectroscopy, and chemical analysis were used. The analysis details were as outlined in the previous work on the lanthanum oxide - chromic oxide system (Rubinichik et al., 1969).

Starting oxides had a specific area of 7.4 m^2/g for lanthanum oxide, and 5.4 m^2/g for chromic oxide, which was obtained from decomposition of ammonium dichromate. Pellets were produced for reaction from a 1:1 molar ratio of the starting oxides.

In vacuo reaction began at 600°C, and after 8h, 5% lanthanum chromite had formed, as shown by chemical analysis. The x-ray phase analysis began to show intense chromite formation at 800°C after 6h reaction. A series of kinetic curves were plotted for lanthanum chromite formation in vacuo, between 800-1050°C, and these curves displayed an initial rapid formation of chromite, with a subsequent slow rate of increase with time. There was a large difference between the amount of chromite formed at 900° and 950°C. At this latter temperature the degree of transformation greatly increased and almost 70% conversion was obtained at 1050°C after 8h. It was only during the period of initial rapid formation that a fit of the data to the Janders and Ginstling-Braunstein equations was achieved. It was stated that the fit of data to these equations and the value found for n in the equation $\alpha = 1 - a^{-kt^n}$ indicated that the process was initially diffusion controlled.

The accelerating effects of oxygen on chromite formation were studied under oxygen atmospheres with partial pressures of 150, 200 and 740 mm of Hg, by comparing two reactions: one at 500°C, where chromate and chromite were found, and the other at 900°C, where the only reaction product was lanthanum chromite. At 500°C, increasing the partial pressure of oxygen, increased the yield of chromate (VI) and chromite. The formation of more chromite was attributed to the catalysing effect of chromate (VI) formation, but at 900°C, where there was also an increase in chromite

formation as the partial pressure of oxygen was increased, two possible explanations were advanced. The increase in yield was due, either to, the catalysing effect brought about by a change in the defectiveness of the crystal structure, or a change in the mechanism of diffusion between an oxygen atmosphere and vacuo.

The kinetics of lanthanum chromite formation were studied from 500°-700°C; which was the approximate range of stability of the chromate (VI), with a partial pressure of oxygen equal to 200 mm of Hg. The kinetic curves plotted for reaction times up to 8h appeared different in nature from those obtained by Rubinichik et al. (1969) as part of their study of the La_2O_3-Cr_2O_3 system at 1 atmosphere of oxygen. In particular, the relationship between chromate decomposition and chromite formation appeared less clear in this latest investigation, perhaps because here chromite formed at lower temperatures and after shorter time intervals. From temperature dependence plots at times of 30 min., 1h and 4h, the maximum amount of chromate (VI), formed for each, around 600°C.

The results of changes in the rate of formation of chromite with steam present at low pressures, were also given. The maximum rate was obtained at a temperature of 800°C, with partial pressures = 8 and 15 torr.; and at 900°C with partial pressures = 8 and 15 torr.

The reactions in the systems Y_2O_3-Cr_2O_3 and Er_2O_3-Cr_2O_3 were examined in vacuo, at a pressure of 2×10^{-3} torr. (Savchenko and Rubinchik, 1973) in order to examine the pure solid phase

reaction without the complication of the gaseous interaction with the system to form intermediates. A 1 : 1 stoichiometric mixture of the oxides was prepared and pelleted for reaction. The pellets were reacted at temperatures between 950 and 1150°C at intervals of 50°C at holding times of 15, 30, 60, 120, 180, 240, 300 and 420 minutes for each temperature.

Only one product formed in each system, yttrium chromite and erbium chromite. It was stated that the kinetic curves plotted for the reaction showed that at low degrees of interaction a thin layer of reaction product formed which did not destroy the contact between the initial components.

In a kinetic and mechanistic study of the Sm_2O_3-Cr_2O_3 system (Rubinchik et al., 1972) the techniques of x-ray powder diffractometry, infra-red spectroscopy and chemical analysis were used in an analogous way to the study of the La_2O_3-Cr_2O_3 system (Rubinchik et al., 1969). Apart from a general investigation of the kinetics, the effect of a gaseous medium, and the crystal structure of Sm_2O_3 on the rate of reaction were also considered. The oxides were reacted in a 1:1 molar ratio with either the C-type Sm_2O_3 (specific area = $4m^2/g$) or the B-type Sm_2O_3 (specific area = $2m^2/g$) being used.

The initial studies were carried out using x-ray diffraction analysis and this revealed that in vacuo or in an atmosphere of oxygen only the one product, samarium chromite, formed. Using C-type

Sm_2O_3-Cr_2O_3 mixtures in oxygen the line most characteristic of samarium chromite appeared after 6h at 600°C, with the full pattern evident after 8h at 800°C. The intensity of these lines increased as the temperature was raised, although the lines of the oxide remained at 1000°C. In vacuo the first appearance of a line due to $SmCrO_3$ did not occur until 850°C and the pattern was not complete until 1050°C, but here there was no marked decrease in the intensity of lines of the oxides indicating a much slower conversion to the chromite.

It was noted that the B form Sm_2O_3 was less reactive than the C-type, with weak lines in the powder diffraction pattern only being observed at 900°C after 8h. Two possible explanations were discounted, the greater surface area of the C-type and the Hedvall effect. The former because the use of a C-type oxide of similar specific area to the B-type used here was no less reactive than previously; the latter because the C-type showed greater reactivity over a range of temperatures not just during the transition C→B. It was also noted that this transition was complete in vacuum at 1000°C, while in oxygen it had only begun at 1050°C; this, it was suggested was another possible reason for the difference in reactivity between vacuum and oxygen. The difference in reactivity between the Band C type Sm_2O_3 was attributed to the larger number of anionic vacancies in the C-type which is characteristic of rare earth oxides of the fluorite type: thus it was stated that the number of diffusing ions and

their mobility will be greater.

On the basis of infra-red spectra the presence of samarium chromate (VI) was shown from 500°C to below 700°C; this finding was confirmed by chemical analysis. Bands in the infra-red from samples of a C-type Sm_2O_3-Cr_2O_3 mixture reacted for 8h at 500 and 600°C were in the correct position to agree with those bands, in the infra-red of (Darrie, 1967) ~~for~~ samarium chromate (VI). The disappearance of bands due to chromate (VI) in the infra-red was explained by decomposition. It is stated that from chemical analysis the maximum of chromate (VI) formation occurred at 500°C after 8h reaction, but here reactions were only carried out at intervals of 100°C.

Kinetic experiments were performed for the temperature range 300-1400°C in air and oxygen, and between temperatures of 850 - 1150°C in argon; both for times between 15 min. and 8h. The curves obtained show only the per cent weight conversion of Sm_2O_3 against time and do not consequently show the separate variation of chromate (VI) and chromite with time.

It was seen that in air or oxygen reaction was essentially complete at 1100°C; while, in vacuum temperatures 200-250°C higher were required to achieve 100% reaction. In air and oxygen the rate of the reaction increased markedly from 600-700°C; but from 700-1100°C, apart from an initial increase in rate of formation below 1h, the subsequent rate was generally very slow with

rise in temperature. This was explained by attributing reaction below 700°C mainly to chromate decomposition with the rate of reaction above this temperature being governed by diffusion through a progressively thickening and well ordered product layer of chromite. It is stated that kinetic data from the beginning of the reaction fitted the Jander equation and an activation energy was calculated. This value, which was not given, and the effect of the crystallinity of the Sm_2O_3 oxide on the reactivity of the system were produced as evidence for a surface diffusion of Sm_2O_3.

In an investigation of the formation of samarium chromite from the reaction of samarium salts with chromic oxide (Prokudina et al., 1972) the prepared salts $Sm_2(C_2O_4)_3.8.3H_2O$, $Sm_2(CO_3)_3.3H_2O$ and $Sm(NO_3)_3.4.6H_2O$ were mixed in a 1:1 molar ratio of the oxides, i.e. 1Sm: 1Cr, with Cr_2O_3 A.R. and pelleted for reaction. The customary techniques of x-ray phase analysis, infra-red spectroscopy and chemical analysis were used to determine the nature of the products.

In the system containing the oxalate salt reaction was considered to begin at 450°C. This was shown by bands in the infra-red spectra in accordance with those of Darrie (1967) for the spectra of the samarium chromate (VI) and by lines in the x-ray diffraction pattern. There was no sign of Sm_2O_3 under these circumstances; therefore, it was concluded that reaction took place between the decomposing oxalate and the chromic oxide directly according to the

equations:-

$$2(Sm_2O_3.CO_2) + 3Cr_2O_3 + {}^9/_2 O_2 \rightarrow 2Sm_2(CrO_4)_3 + 2CO_2$$

$$2Sm_2O_3.CO_2 + 3Cr_2O_3 + {}^9/_2 O_2 \rightarrow 2Sm_2(CrO_4)_3 + CO_2.$$

From the chemical analysis data the maximum of chromate formation occurred at 600°C, thereafter increasing temperature promotes decomposition of the chromate with formation of chromite. The x-ray and infra-red data suggested that formation of $SmCrO_3$ took place in the temperature range 700-1000°C.

At 700°C the x-ray diffraction pattern showed lines of C-type Sm_2O_3, the decomposition product of the oxalate; thus, it is assumed that $SmCrO_3$ was also formed by direct reaction of the oxides, the total process is represented by the equations below:-

$$2Sm_2(CrO_4)_3 \rightarrow 4SmCrO_3 + Cr_2O_3 + 9/2O_2 \qquad (1)$$

$$Sm_2O_3 + Cr_2O_3 \rightarrow 2SmCrO_3 \qquad (2)$$

Reaction (1) was considered to occur up to approximately 700°C, where the chromate (VI) was stable and reaction (2) at higher temperatures where no chromate (VI) was apparent. Complete conversion to the chromite was obtained at 1000°C after 6h.

In the system $Sm_2(CO_3)_3$-Cr_2O_3 no intermediate was detected and reaction occurred largely by direct interaction of the oxides. This process was followed analytically by determination of unreacted lanthanide oxide. The reactions at 700 and 800°C used both pellets and powders and it was found that powders gave slightly more product at each time than pellets. This was explained by easier

penetration of oxygen to the reaction site. Prokudina and associates are inconsistent here in applying kinetic equations, because of the absence of chromate (VI), yet using its formation to explain this result.

The $2Sm(NO_3)_3$-Cr_2O_3 system was much more reactive. Reaction began at 300°C with the production of $Sm_2(CrO_4)_3$, and this increased in amount to 450°C. Above this temperature $SmCrO_3$ formed, and at 700°C, 100% formation of chromite was achieved.

The formation of samarium chromite from the reaction of the co-precipitated samarium (III) and chromium (III) hydroxides (Rubinchik et al., 1972) was also examined. Here reaction commenced at 400°C forming only $SmCrO_4$ amd between 400 and 600°C this was the only reaction product. At 650°C the samarium chromate (V) decomposed to the chromite, liberating oxygen.

In an analogous study of the formation of lanthanum chromite (Rubinchik, 1973) from the co-precipitated lanthanum (III) and chromium (III) hydroxides, the hydroxides were pelleted for reaction and then heated at intervals of 100°C between 100 and 1200°C for periods of 6h. The investigation of products formed was conducted using x-ray powder photography and infra-red spectroscopy.

An initial interaction of the hydroxides may have taken place at temperatures of less than 200°C, but at 300°C x-ray data indicated the presence of $LaCrO_4$, and this was confirmed by comparison of the infra-red data, with the infra-red data of Darrie and Doyle

(1967). It was also stated that two phases lanthanum chromate (V) and lanthanum chromate (VI) were present in the range 300-400°C; while at 500°C there was evidence for links of $LaCrO_4$ and $LaCrO_3$, with complete formation of chromite occurring at 700°C after 6h.

No oxides were detected, therefore the formation of chromite was considered to occur only from decomposition of the chromates. D.T.A. evidence shows minima at 450° and 650°C, which were attributed to the decomposition of the $La_2(CrO_4)_3$ and $LaCrO_4$. To describe the processes involved the following equations were used:-

1) $La(OH)_3.xH_2O + 3Cr_2O_3.yH_2O + 3/2O_2 \xrightarrow{300\text{-}400^\circ C} 2La_2(CrO_4)_3 + 2H_2O$

2) $2La_2(CrO_4)_3 \rightarrow 4LaCrO_4 + 5/2O_2 + Cr_2O_3$

3) $4LaCrO_4 \rightarrow 4LaCrO_3 + 2O_2$.

In vacuo, using precipitated hydroxides, prepared initially from nitrates, which give off oxygen during decomposition, there was little difference between reaction in vacuo and in air. With the hydroxides prepared from chlorides, where no oxygen was given off, and no chromate forms, the temperature required for complete formation of the chromite rises to 1000°C and the reaction can be simply represented by the equation:-

$$La_2O_3 + Cr_2O_3 \rightarrow LaCrO_3$$

It was stated that reaction with a mechanical mixture of nitrates gave one product $La_2(CrO_4)_3$ stable up to 1000°C, only after which did formation of lanthanum chromite occur, c.f. Schwarz,

1963, where the mixtures of nitrates were obtained from solution to prepare the chromates (V).

It was concluded that differences in reactivity had little to do with specific area of surfaces, much more important was the formation of intermediates.

These studies of the mechanism of chromite formation where salts or co-precipitated hydroxides have been used present a different set of physical and chemical conditions from those encountered in the reaction of the lanthanide (III) oxides and chromium (III) oxide and were in some ways akin to the study of preparative reactions, c.f. Schwarz, 1963, where he used hydroxides and other salts to prepare the chromates (V) around 600°C.

The Nd_2O_3-Cr_2O_3 system has been studied in some detail. This system was studied (Savchenko et al., 1973) using both A and C-type Nd_2O_3, in vacuo p = 10^{-3} mm Hg, and in an atmosphere of oxygen. The specific surfaces of the neodymium oxide were 1.8 m^2/g for A Nd_2O_3, 3.8 m^2/g for C-type Nd_2O_3 and 3.3 m^2/g for the chromic oxide used. The mixtures were prepared of the oxides in 1:1 molar ratios and pellets were produced under pressure for subsequent reaction.

To determine the products x-ray diffractometry and infra-red spectroscopy were used principally; while the extent of reaction was monitored by dissolving unreacted Nd_2O_3 in a 25% solution of ammonium acetate and then titrating to determine the

amount. Chromate was also detected, or perhaps determined, by titration, for here the text was ambiguous.

In oxygen the formation of a product of oxidation state greater than 3, determined from chemical analysis, was a significant feature of this system. Infra-red evidence confirmed this with three intense bands between 890 and 935 cm^{-1} and another less intense band at 850 cm^{-1}, which ~~was~~ were characteristic of the CrO_4^{2-} ion. The slight difference in band shape between this, and the chromate (VI) obtained from precipitation, was accounted for, by a small change in the shape of the CrO_4^{2-} ion, caused by different conditions of synthesis. Additional confirmation for the presence of chromate (VI) was obtained from a comparison of the ultra-violet diffuse reflectance spectra of precipitated $Nd_2(CrO_4)_3$, with mixtures of oxides calcined in the range 660-800°C, and those mixtures not containing chromate (VI).

From kinetic plots the chromate increased gradually at temperatures of 600 and 650°C and reached a maxima on the curves for temperatures 700 and 800°C. It was noted that the initial decomposition of neodymium chromate (VI) coincides with the acceleration of the rate at which chromite is formed, at a temperature of 700°C. Therefore, it was stated that the generation of this oxidised intermediate could help explain why the formation of $NdCrO_3$, in vacuo, began at a temperature 300-350°C higher than in an oxygen atmosphere, and subsequently reacted to a lesser extent.

A comparison of the reactivities of A and C type Nd_2O_3 indicated that the C-type was the more reactive, and it was suggested that the C-type with a larger surface and therefore a greater area of contact also, less dense and more porous than the A-type could afford greater mobility to a larger number of ions. The possibility of the Hedvall effect for the transition C→A being responsible was discounted, since the transition was not observed.

The difference in reactivity between the A and C type could explain the sharp decrease in the rate of formation of $NdCrO_3$ at temperatures of 900°C and above observed in the A-Nd_2O_3 system. The presence of the A-form in mixtures of both forms slows down the interaction process.

While the kinetic curves in oxygen were obtained in the temperature range 600-1000°C, those in vacuum were plotted at temperatures between 1050 and 1150°C; and, in vacuo, because of the fit of experimental data to the Janders equation it was concluded that reaction was limited to diffusion only. Here the reaction mechanism because of the close agreement of activation energies, was considered to be similar for both A and C-type Nd_2O_3.

An experiment in which pellets of Nd_2O_3 and Cr_2O_3 were placed 1-1.5mm apart and heated at a temperature of 650°C was performed to indicate the importance of gaseous diffusion of the ions. That side of the A-Nd_2O_3 pellet nearest the Cr_2O_3 sample was

covered with a yellow coating. The infra-red of the yellow solid showed the absorption bands of neodymium chromate (VI). Thus it was ascertained that the chromate (VI) was formed through transfer of surface oxidised Cr_2O_3 to the surface of Nd_2O_3. The following reactions were postulated as occurring in an oxygen atmosphere:-

$$Cr_2O_3 + XO_2 \rightarrow Cr_2O_{3+X}$$

$$Cr_2O_{3+X} + Nd_2O_3 \rightarrow Nd_2(CrO_4)_3$$

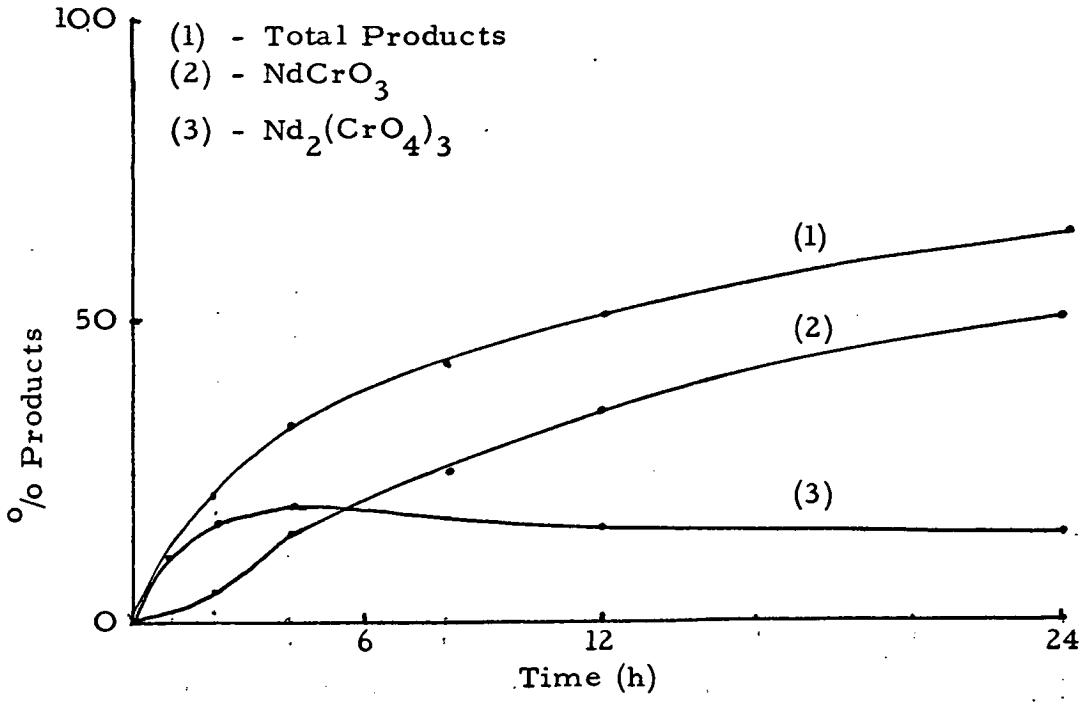
$$Nd_2(CrO_4)_3 \rightarrow 2NdCrO_3 + \tfrac{1}{2}Cr_2O_3 + 9/4\,O_2$$

$$Cr_2O_3 + Nd_2O_3 \rightarrow 2NdCrO_3.$$

In vacuo only the process represented by the final equation above occurs.

Completely independent, the most detailed and exhaustive study of any lanthanide (III) oxide - chromic oxide system was undertaken by Gibb (1973). A complete identification of all possible products and reactants and a determination of their respective amounts was used to study the kinetics and mechanism of the Nd_2O_3-Cr_2O_3 system under a variety of conditions. The A-type polymorph of Nd_2O_3 was used throughout. Reactant mixtures were prepared from commercially available oxides of high purity and were normally pelleted for reaction using 0.4g of the reactant mixture.

The isothermal kinetics were studied at various temperatures and the diagram below showing the results at 650°C is representative of those obtained in the range 630-720°C.



In this system only the one intermediate, $Nd_2(CrO_4)_3$, stable in air from approximately 350°C to approximately 800°C, was formed; in addition to the thermally stable chromite compound. As the temperature was raised the isothermals exhibited the following trends. The initial rate of formation of chromate (VI) increased, but the initial rate of decomposition, also increased, thus the maxima of chromate formation appeared at shorter reaction times. The period in which the initial rate of formation of chromite increased with time shortened with rise in temperature, and there was no acceleratory period evident above 685°C. The total products generally increased with temperature and their isothermal plots all showed a rate of formation, which decreased with time.

The variation of product with time was also studied at higher temperatures. In the isothermal at 760°C only a small amount of chromate was present; while at 900°C there was no chromate present, and at this temperature the formation of chromite, although initially rapid, subsequently increased very slowly with time.

The effect of temperature in this system was also studied at fixed times; for 1h between 630 and 880°C in air, and at 2h in the range 630-800°C in oxygen. In air the maximum of chromate (VI) formation occurred at 680°C, with only a small amount remaining at 800°C. The amount of $NdCrO_3$ formed increased rapidly from 650°C to a maximum at 760°C, and then decreased markedly up to 840°C. There was a slight increase in chromite formed from 840 to 880°C. In oxygen, however, no decrease in the amount of chromite was observed with increasing temperature, and the rate of formation of chromite, which was rapid throughout the temperature range studied, increased with temperature below 700°C, and decreased above this temperature. At 800°C a 91.5% yield of chromite was obtained. In oxygen the maximum of chromate formation was reached at 650°C and above this temperature the amount of chromate decreased, rapidly to 720°C, and more slowly from 720-800°C.

A comparison of reactions in air and oxygen showed that invariably chromate (VI) attained higher yields in oxygen, and

although, initially chromite appeared to form at lower temperatures in air, hence in greater amount, at temperatures above 600°C, chromite was always present in higher yield in oxygen. It was also noted that the rate of formation of neodymium chromate (VI) and its subsequent decomposition to chromite were enhanced in an oxygen containing atmosphere.

The effect of powders and pellets of differing width on the reaction was also investigated, but the results were not clear cut; although it was stated that with powders the amount of chromate (VI) produced was more, and the yield of chromite formed less than that found in reaction of pellets.

To examine the possibility of chromite formation without the presence of an intermediate chromate (VI) compound, three reactions were carried out in an argon atmosphere all for a period of 3h, two at 660°C and one at 1000°C. In either case, it was reported that no reaction occurred. On this basis it was concluded that formation of chromite took place by chromate decomposition alone even at temperatures up to 1000°C, but for this to be so required the postulation of a very precise relationship between chromate formation and decomposition.

The main result to emerge from the physical data, which could not be shown by chemical analysis was from infra-red evidence, which showed no anion-anion coupling of the chromate (VI) produced in the solid-state, unlike that prepared from solution. Thus, this

structural difference, it was stated, could account for the greater thermal stability of the chromate produced in the solid state, the exact structure of which remains unknown.

In the present work, the systems La_2O_3-Cr_2O_3, Y_2O_3-Cr_2O_3 and Pr_2O_3-Cr_2O_3 were studied by following either, the variation of products, with time, or temperature; using chemical analysis to determine the amounts of the individual products. This, it was hoped, would enable, from the kinetics and temperature dependence characteristics of reaction carried out in air, oxygen and argon atmospheres; the elucidation of the processes involved in these reactions between solid oxides.

STANDARD EXPERIMENTAL TECHNIQUES

Both physical and chemical methods were used to investigate the nature of the reaction in the solid state for the La_2O_3-Cr_2O_3 system; but only chemical methods were used for the systems Y_2O_3-Cr_2O_3 and Pr_2O_3-Cr_2O_3. This section describes the physical and chemical techniques employed, and relevant experimental details other than results.

Physical Techniques

Infra-red spectroscopy, ultra-violet diffuse reflectance spectroscopy, x-ray powder diffraction patterns and measurements of magnetic susceptibility have all been used to study reactions in the La_2O_3-Cr_2O_3 system, or to characterise the reactants of, and the possible products in, this system.

Infra-red spectra were obtained using a Perkin-Elmer 457 spectrophotometer, which records in the range 4000 cm^{-1} to 250 cm^{-1}. Nujol mull and KBr disc methods of sample preparation were used. A satisfactory KBr disc for spectroscopy was obtained in the following way. Approximately 1% by weight of sample was added to enough KBr of spectroscopic quality, which had passed mesh 200, and the mixture intimately ground for five minutes. The mixture was then transferred to a Perkin-Elmer 13mm. dye where, under a pressure of 8 tons/sq.in., a pellet is formed, ideally 1mm thick.

To enable ultra-violet diffuse reflectance spectra to be

measured a Unican S.P. 500 spectrophotometer was used in conjunction with an S.P. 540 diffuse reflectance attachment. Sample preparation is important, as reference material and diluent magnesium oxide was used. In diluting, 0.003 mole of sample was mixed with enough magnesium oxide to bring the total weight to 2g., though the correct ratio varies with the molecular weight of sample and its individual intensity of absorption. It was necessary to ensure the perfectly smooth non-compacted surface, essential to good spectra.

X-ray powder diffraction data were recorded, using a Philips vacuum sealed x-ray tube as the emitting source of CuKα radiation, λ = 1.5418Å, on a Philips P.W. 1051 powder diffractometer unit, between values of 2θ; 4° to 50°.

Measurements of magnetic susceptibility by the Gouy method were made on a Stanton S.M. 12 semi-micro balance using a Newports instruments 4" water cooled electromagnet. The calibrant used was mercuric tetra thiocyano cobaltate. Calculations used the Figgis and Lewis (1960) formulation.

Chemical Techniques

Before the description of the analysis scheme used (Gibb, 1973) and the procedural alterations for the La_2O_3-Cr_2O_3 system, together with the modifications for the systems Y_2O_3-Cr_2O_3 and Pr_2O_3-Cr_2O_3, a summary of the preparations of some expected products are given, the main reason for whose synthesis is their use in testing the aforementioned analytical procedure.

Lanthanum chromate (V) ($LaCrO_4$) was prepared by Schwarz's method (Schwarz, 1963) in which a stiochiometric mixture of the nitrates is a preliminary stage of the preparation. A new way of obtaining chromium(III)nitrate was used. Approximately 2g. of chromium oxide were dissolved in 25ml. distilled water and 25ml. concentrated hydrochloric acid and 30ml. of ethanol were added. The whole was evaporated to a small volume to give a dark green solution, which was then diluted to 100ml. and the process repeated twice more to remove excess hydrochloric acid and any ethanol which might have remained. The chromium chloride was converted to the nitrate by addition of excess 50% nitric acid and by a thrice repeated process of evaporation a dark green viscous solution of chromium nitrate was obtained. Lanthanum nitrate was prepared, essentially free of excess nitric acid, by the dissolution of a stoichiometric quantity of lanthanum oxide in the minimum of 50% nitric acid and by twice, consecutively diluting with distilled water then evaporating to a small volume. The solution of the mixture of the two nitrates was further reduced in volume, then diluted and finally evaporated to a paste. The paste was heated at 250°C until a black flaky solid had been formed, which when ground was heated at 580°C for one hour in an atmosphere of oxygen. This was then reground and the procedure repeated every two hours for a total of eight hours.

Lanthanum chromate (VI) ($La_2(CrO_4)_3 \cdot 7H_2O$) as the hepta-

hydrate was prepared by its precipitation from a solution of a stoichiometric mixture of aqueous chromium trioxide and lanthanum nitrate by dropwise addition of dilute sodium hydroxide until pH 5-6.5 was reached (Schwarz, 1963). Anhydrous lanthanum chromate (VI) was obtained by heating the hepta-hydrate at 300°C for one hour.

Lanthanum chromite ($LaCrO_3$) was formed as the product of the solid state reaction between a 1:1 molar ratio of lanthanum (III) oxide and chromium oxide (Cr_2O_3). The two oxides were intimately ground and mixed, and then 1g. of the mixture was pelleted by applying a pressure of 10 tons/sq.in. to a KBr dye. The pellets were heated at 1000°C for two hours. The lanthanum chromite so produced was brown. Although generally, the two oxides were pre-sintered before mixing the reactivity was enhanced without pre-calcination when reaction was completed in a few hours at 700°C. In either case reaction was essentially 100% after 2 hours reaction at 800°C. Previous methods of preparation required pelleting then heating at 1200°C for one hour and subsequently heating at 1000°C for 24 hours.

Praesodymium chromate (V) ($PrCrO_4$) was obtained in a similar manner to that for lanthanum chromate (V).

Table A gives the results of the chemical analysis for these compounds.

TABLE A CHEMICAL ANALYSIS OF SOME CHROMATES AND CHROMITES

Compound	°/o Ln		°/oCr		°/o H_2O	
	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.
$La_2(CrO_4)_3.7H_2O$	36.95	36.98	20.75	20.74	16.77	16.71
$La_2(CrO_4)_3$	44.40	44.82	24.92	24.84		
$LaCrO_4$	54.50	54.63	20.40	20.36*		
$LaCrO_3$	58.15	57.98	21.76	21.75		
$PrCrO_4$	54.85	54.60	20.24	20.30*		

The determination of °/o chromium with an asterisk (*) refers to the calculation of the chromium content by the method of Darrie, 1967. By this method to account for the disproportionation of the chromate (V) the arithmetical expedient of multiplication by 1.5 is used.

Analysis in the La_2O_3-Cr_2O_3 system

The analysis scheme for the La_2O_3-Cr_2O_3 system, together with alterations from Gibb (1973) is given below. The reasons for the alterations are given later in the text. Determination by indirect analysis of the starting oxides and the products lanthanum chromate (VI), lanthanum chromate (V) and lanthanum chromite were made possible by this scheme. To enable this to be done five experimental parameters known as, soluble lanthanum, insoluble lanthanum, insoluble chromium, soluble chromium and total soluble chromium were required, where soluble and insoluble refers to the

behaviour on addition of concentrated hydrochloric acid. A determination of total soluble chromium was necessary in addition to that for soluble chromium because of the disproportionation:-

$$3CrO_4^{3-} + 8H^+ \rightarrow 2CrO_4^{2-} + Cr^{3+} + 4H_2O.$$

The effects of this disproportionation were obviated in a way which will be more fully explained later, by reducing all the chromium to oxidation state (III), then by oxidising all the chromium to oxidation state (VI). Soluble lanthanum was obtained from lanthanum oxide, lanthanum chromate (VI), and lanthanum chromate (V), while the only source of insoluble lanthanum was from lanthanum chromite. Insoluble chromium was obtained from the chromic oxide and lanthanum chromite. Soluble chromium and total soluble chromium were required to determine the product ratio of lanthanum chromate (VI) and lanthanum chromate (V), where there arose the possibility of formation of both these products.

Three sets of duplicates were required. Soluble chromium was determined from one of these sets as follows. To between O.15g-O.2Og. of sample were added 25ml. 2N hydrochloric acid. Five minutes were allowed for chromium to dissolve, which followed by filtering through porosity 4 sintered glass crucibles into a filter flask already containing 150ml. distilled water, ensured immediate dilution. The chromate was further diluted to 250-300ml. before addition of 2g. potassium iodide and titration with approximately O.025N sodium thiosulphate.

Total soluble chromium was obtained from the filtrate of a second set of duplicates of weight approximately O.25-O.3Og. Here after adding 25ml. 2N hydrochloric acid and stirring for 2O minutes the solution was filtered through a Whatmans' No. 42 filter paper. The insoluble material was discarded. The solution was diluted to 2OOml. and 15ml. ethanol were added and the whole was evaporated to a small volume, during which time all the chromium was reduced to chromium (III) and the ethanol removed. The green solution was diluted to 2OOml., and on addition of 12g. ammonium chloride, and 3.5g. potassium cyanate, the whole was gently heated to boiling to initiate precipitation of chromium hydroxide. Decantation of the supernatant liquid through a Whatmans' No. 41 filter paper was followed by washing the precipitate with a hot, slightly ammoniacal, solution of ammonium nitrate (4g./lOOml.), and by this means the precipitate was transferred to the filter paper. The flask was rinsed three times with hot ammonium nitrate then filtered as above. The flask was cleaned by addition of a few drops hydrochloric acid placed down the side, where alizarin was used to indicate the change in pH necessary, on addition of ammonium hydroxide, to precipitate a small amount of chromium hydroxide. The filtrate was boiled and alizarin added. The pH was adjusted by adding a few drops of concentrated hydrochloric acid, enough to turn the filtrate yellow, then adding the minimum amount of ammonium hydroxide to effect a colour change, and produce a fine precipitate of chromium hydroxide.

This was then filtered through Whatmans' No. 42 filter paper to which was added the further small precipitate obtained from cleaning the flask. The filter papers were burned in a porcelain crucible, and to bring the residue which contains all the chromium from lanthanum chromate (VI) and lanthanum chromate (V) into a solution of chromium (VI) : a mixture of the residue with 2g. sodium peroxide was heated until molten, and when cool, this was leached with hot distilled water. The basic solution and precipitate were boiled for 30 minutes to ensure the removal of excess peroxide, and filtered through a sintered glass crucible, porosity 3. The cooled basic chromium (VI) solution was diluted to 250ml. and approximately 18ml. hydrochloric acid were added to render the solution acidic. 2g. of potassium iodide were added and the chromium was determined iodometrically, titrating with O.025N sodium thiousulphate (amended Vogel, 1954).

From the remaining duplicate of analyses, weighing approximately O.25-O.3Og., soluble lanthanum, insoluble lanthanum and insoluble chromium were determined. As before 25ml. 2N hydrochloric acid were added to each of the reacted samples, and allowing 20 minutes for the complete dissolution of unreacted lanthanum (III) oxide, lanthanum chromate (VI) and lanthanum chromate (V), the solution was separated from the insoluble chromic oxide and lanthanum chromite by filtering through Whatmans' No. 42 filter paper.

From the solution soluble lanthanum was obtained. The filtrate was diluted to approximately 180ml., and with stirring, sufficient hot oxalic acid solution was added dropwise until the resulting solution was approximately O.2ON in hydrochloric acid and O.5ON with respect to oxalic acid. During which time precipitation began, and to ensure complete precipitation of the lanthanum oxalate decahydrate, stirring was continued for a further two hours. The precipitate was collected on Whatmans' No. 41 filter paper, washed with a O.2ON solution of oxalic acid and then transferred to a weighed silica crucible. After burning off the filter papers there remained the lanthanum oxide, which to ensure the complete decomposition of the oxalate was calcined at a temperature around 900°C for 30 minutes. The soluble lanthanum was weighed as lanthanum (III) oxide (Duval, 1948).

The insoluble material, filtered as above, contained either or both chromic oxide and lanthanum chromite. They were obtained free of filter paper in a porcelain crucible by burning off the ashless filter papers. The residue was mixed with approximately 2g. sodium peroxide and heated until molten. This, when cool, was leached with hot distilled water to obtain a basic solution of chromate (VI), and lanthanum hydroxide as precipitate. To remove excess peroxide the solution and precipitate were boiled for 30 minutes and filtered through porosity 3 sintered glass crucibles. After cooling, the solution was diluted to 250ml. and acidified with 18ml.

concentrated hydrochloric acid. 2g. of potassium iodide were added and the solution titrated with approximately O.O5N sodium thiosulphate, to determine the insoluble chromium.

The precipitate containing lanthanum hydroxide was dissolved by adding 6ml. hydrochloric acid, and then diluted immediately to 3Oml. The solution containing lanthanum chloride was diluted eventually to 2OOml., then boiled and filtered through Whatmans' No. 41 filter paper. The solution was again diluted to approximately 2OOml. and the lanthanum oxalate decahydrate precipitated as already described for the soluble lanthanum. The procedure was then identical to that for soluble lanthanum and the insoluble lanthanum was determined gravimetrically as lanthanum (III) oxide.

It was necessary to test the analysis scheme and to establish criteria of precision and accuracy. The most satisfactory way of checking the analysis scheme was the use of synthetic mixtures containing reactants and products, where the constituents were present in approximately equal amounts by weight.

Although this allows the accuracy of each part of the analysis to be determined, the mixture differs significantly, from reacted samples, as regards the topography and distribution of product. Therefore in a reacted sample other analytical problems not encountered in the use of synthetic mixtures may be evident.

To interpret results from synthetic mixtures and subsequently

to have criteria with which the precision of the analyses, of samples from reaction, could be judged, errors and their estimation were considered in detail.

Errors : their estimation and combination

The following rules were used:

1) Addition or substraction. The absolute errors were added, the relative errors $\mathcal{E}$ were obtained from $\mathcal{E} = {}^{d}/_{M}$ (where M = the true value) was taken to be the mean, $\bar{X}$.

2) Multiplication or division. Add the relative error $\mathcal{E}$; $|d|$ was obtained from the equation above.

3) When multiplying by a constant, $|d|$ is multiplied, $\mathcal{E}$ is not so multiplied. Also, $d = |M-x|$, where as above M = true value, x = observed value. As an approximation $\mathcal{E} = {}^{d}/_{\bar{X}}$, the correctness of this approximation increases with the number of single determinations made.

In the final result the relative maximum error was given by:-

$$\mathcal{E}p = \mathcal{E}x_1 + \mathcal{E}x_2 + \mathcal{E}x_3 \ldots\ldots \sum_{1}^{j} \mathcal{E}x_j$$

It was considered unlikely that individual errors would combine in such a way as to give the maximum possible error. To partially correct this the empirical rules given below were used.

Sums and differences: $A(|d| = a) \pm B(|d| = b) = C(|d| = c)$

$$C|d|_{\text{total}} = \sqrt{a^2 + b^2}$$

Multiplication and division: $A(|d| = a) \times B(|d| = b) = C(|d| = c)$

or $\frac{A(|d| = a)}{B(|d| = b)} = C(|d| = c)$

Then the rule was $\varepsilon_c = \sqrt{\varepsilon_a^2 + \varepsilon_b^2}$

Limits of accuracy of equipment

The magnitude of errors were in part based on the data supplied by manufacturers or from Eckschlager (1969).

Weighings	Absolute error d in mg.
Load maximum 20g.	0.20mg.
Load 20g. - 50g.	0.50mg.

Titrations (with 50ml. grade A burette)	Absolute error d in ml.
If blank done	$\pm$0.1ml.
If no blank done	$\pm$0.12ml.
	(in the above reading error taken to be 0.025ml.)

Pipette	Absolute error d in ml.
25ml.	Grade A 0.061
50ml.	0.077

Volumetric flasks	Absolute error (d) in ml.
250ml.	Grade A. 0.330
500ml.	0.600
1000ml.	0.900

Synthetic mixtures were then used to check the

accuracy of the technique and the scheme. The treatment of errors and their magnitude as given above allowed an estimation of the accuracy with which the experimental parameters could be determined. These could be used in a comparison with the actual accuracy to indicate any possible defects in the analysis scheme.

The calculation below shows how the estimation of accuracy was applied to a synthetic mixture analysed by the unaltered analysis scheme.

Estimation of the accuracy for a synthetic mixture (using unamended technique)

The empirical treatment of error combination and the magnitude of errors allowed the calculation of absolute errors involved in a) Weighing initial sample, b) Titrations, c) Weighing of precipitated lanthanum oxide.

a) The absolute error in weighing $|d_w|$ was given by $\sqrt{2(0.0005)^2}$ = 0.0007g.

b) The absolute error in titration $|d_m|$ for titres less than 50ml. was given by $\sqrt{[2(0.025^{\&1} + (0.05)^2]}$ ml. = 0.061ml.

c) The absolute error in weighing precipitated lanthanum oxide $|d_{ppt}|$ was given by $\sqrt{4(0.0002)^2}$ g. = 0.0004g.

The relative °/o error in weighing ($\mathcal{E}w$) is given by

$$\frac{d_w}{\text{wt. of sample}} \times 100$$

The relative °/o error in titration ($\mathcal{E}_{tr}$) is given by

$$\frac{d_{tr}}{\text{titration in ml.}} \times 100$$

The relative $^{o}/o$ error in weighing precipitate ($\mathcal{E}_{ppt}$) =

$$\frac{d_{ppt}}{\text{wt. of sample}} \times 100$$

(The relative percentage error in standardisation for the sodium thiosulphate used in the titration $\mathcal{E}_{std}$ was calculated to be $0.79^{o}/o$.)

The table below shows the weight of samples and the experimental determinations for weighings of precipitate and titrations where applicable.

Experimental parameter	weight of sample		titrations(ml)		weight of precipitate	
	A	B	A	B	A	B
Soluble chromium	0.1272g.	0.1312g.	17.28	17.93	-	-
Insoluble chromium	0.1272g.	0.1312g.	61.85	63.30	-	-
Soluble lanthanum	0.1010g.	0.1021g.	-	-	0.0397g.	0.0400g.
Insoluble lanthanum	0.1272g.	0.1312g.	-	-	0.0193g.	0.0206g.

From these values were found the respective relative percentage errors and from these were determined the total percentage error $\mathcal{E}_{T}$.

For soluble and insoluble chromium $\mathcal{E}_{T} = \sqrt{(\mathcal{E}_{std})^2 + (\mathcal{E}_{w})^2 + (\mathcal{E}_{tr})^2}$

For soluble and insoluble lanthanum $\mathcal{E}_{T} = \sqrt{(\mathcal{E}_{w})^2 + (\mathcal{E}_{ppt})^2}$

These are shown in the table below:-

Experimental parameter	$\mathcal{E}_w$	$\mathcal{E}_{ppt}$	$\mathcal{E}_{std}$	$\mathcal{E}_{tr}$	$\mathcal{E}_T$
Soluble chromium	0.54	-	0.79	0.35	1.02
Insoluble chromium	0.54	-	0.79	0.20	0.98
Soluble lanthanum	0.69	1.01	-	-	1.22
Insoluble lanthanum	0.54	2.01	-	-	2.08

The estimated accuracy is given in table B, together with the results, the actual accuracy and the precision.

Table C also gives the analysis results of a synthetic mixture using the unamended scheme.

TABLE B Analysis of a synthetic mixture containing lanthanum chromate (VI), lanthanum chromite, lanthanum oxide and chromic oxide.

	Results				Precision		Accuracy	
	A	B	$\bar{X}$	Calc.	δ	$S/\bar{X}$	$(\mathcal{E}_{est})$	$(\mathcal{E}_{act})$
soluble lanthanum	33.52	33.40	33.46	33.92	0.06	0.18	1.22	1.36
soluble chromium	5.97	6.01	5.99	6.40	0.02	0.33	1.02	6.40
insoluble chromium	21.39	21.23	21.31	21.84	0.08	0.38	0.98	2.43
insoluble lanthanum	13.27	13.39	13.33	13.63	0.06	0.45	2.08	2.20

TABLE C Analysis of a synthetic mixture containing lanthanum chromate (VI), lanthanum chromate (V), lanthanum oxide and chromic oxide.

	Results				Precision		Accuracy °/o	
	A	B	$\bar{X}$	Calc.	δ	$\delta/\bar{X}$ °/o	($\mathcal{E}_{est}$)	($\mathcal{E}_{act}$)
Soluble lanthanum	44.11	43.75	43.93	44.56	0.18	0.41	1.10	1.41
Soluble chromium	9.43	9.37	9.41	9.69	0.04	0.22	1.09	2.79
Insoluble chromium	18.26	18.28	18.27	18.34	0.01	-	1.02	0.38
Total soluble chromium	11.33	11.10	11.22	11.39	0.04	0.85	0.96	1.40

These analyses show that although the precision of results as defined above is adequate there are large differences between the estimated and actual accuracy. The largest disparity occurred, almost without exception, for the determination of soluble chromium in all analyses of synthetic mixtures, while those for insoluble chromium and total soluble chromium were generally less, but variable, and frequently significant.

The insoluble lanthanum and soluble lanthanum determinations were close in value to the estimated accuracy but here the estimated value itself, in nearly all cases over 1°/o, was considered too large. This error could be reduced by increasing the initial weight of sample and in future analyses this was done.

There remained the problem of the significant discrepancy between the estimated and actual accuracy for chromium determination. These parts of the analysis were considered in detail to understand the reasons for, and find the sources of the errors, and rectify them.

Previously, as in the synthetic mixtures, shown in tables B and C, soluble chromium was determined in the following manner. Approximately O.15g. of sample were extracted with 25ml. 2N. hydrochloric acid during a period of 2O minutes, with gentle stirring, and then the chromate (VI) solution was filtered through Whatmans' No. 42 filter paper to remove insoluble material. The total process took at least 2 hours, but it was found that in a solution of 2N hydrochloric acid, even after 15 minutes, the chromate (VI) was being reduced to chromium (III) with concomitant oxidation of chloride ion to chlorine. To remedy this while still using a cognate method it was necessary to bring the soluble chromium into solution as soon as possible. This was done as already described by decreasing extraction time to 5 minutes and filtration time to again approximately five minutes, while ensuring immediate dilution.

Insoluble and total soluble chromium are present in a basic solution as chromate (VI) before acidification; and although their respective E°_{s} values for the system would not indicate, unlike those for the acidic solution, the possibility of the reduction of chromate (VI), this was also checked. The results showed that chromium (VI)

was stable, at least for several days, in a basic solution formed after a sodium peroxide fusion, but here again it was necessary after acidification, to titrate immediately.

After this problem had been realised and corrected, other synthetic mixtures were prepared to test the amended technique. The analysis results for two of these are given in tables D and E.

The synthetic mixture in table D contained 16.56°/o lanthanum chromate (VI) heptahydrate, 23.07°/o lanthanum chromate (V), 28.72°/o chromic oxide, and 31.65°/o lanthanum (III) oxide. This did not involve testing the accuracy of the insoluble lanthanum.

TABLE D Analysis of a synthetic mixture containing lanthanum chromate (VI) heptahydrate, lanthanum chromate (V), lanthanum oxide and chromic oxide.

	Results					Accuracy °/o		Precision	
	A	B	$\bar{X}$	Calc.	Id	E_{act}	E_{est}	δ	$\delta/\bar{X}$(°/o)
Soluble chromium	6.57	6.60	6.58	6.58	.021	00	.37	0.02	0.30
Insoluble chromium	19.60	19.51	19.55	19.65	.072	0.51	.37	0.05	0.26
Soluble lanthanum	45.21	45.30	45.26	45.48	.029	0.48	.26	0.05	0.11
Total soluble chromium	7.93	7.96	7.95	7.97	.118	0.13	.36	0.02	0.25

The analysis results give:-

$La_2(CrO_4)_3.7H_2O$	$LaCrO_4$	$LaCrO_3$
16.84 ± 0.56%	22.68 ± 0.57%	-

La_2O_3	Cr_2O_3	Total
31.52 ± 0.41%	28.57 ± 0.09%	99.61 ± 0.9%.

The synthetic mixture in table E contained by weight 24.48% lanthanum chromate (V), 14.89% lanthanum chromate (VI) heptahydrate, 15.39% lanthanum chromite, 20.06% chromic oxide and 25.16% lanthanum oxide. It therefore tested the accuracy of all parts of the analysis scheme.

It should be noted that the lanthanum chromate (V) and chromate (VI) used were not stoichiometric, but that the data obtained from the analysis of the chromates was used to calculate the expected values for experimental parameters.

TABLE E Analysis of a synthetic mixture containing lanthanum chromate (VI) heptahydrate, lanthanum chromate (V), lanthanum chromate (III), lanthanum oxide and chromic oxide.

	Results					Accuracy °/o		Precision	
	A	B	$\bar{X}$	Calc	|d|	ε_{act}	ε_{est}	δ	$\delta/\bar{X}$(°/o)
Soluble chromium	6.43	6.45	6.44	6.42	.023	.31	.36	.01	.16
Total soluble chromium	7.91	7.85	7.88	7.90	.056	.25	.33	.03	.38
Insoluble chromium	16.94	17.01	16.98	17.07	.026	.53	.33	.04	.68
Soluble lanthanum	39.87	39.90	39.88	40.12	.124	.60	.31	.02	.05
Insoluble lanthanum	8.81	8.84	8.83	8.94	.105	1.23	1.19	.02	.23

The analysis results give:-

$La_2(CrO_4)_3.7H_2O$	$LaCrO_4$	$LaCrO_3$
15.40 ± 0.41°/o	23.84 ± 0.53°/o	15.18 ± 0.09°/o
La_2O_3	Cr_2O_3	Total
25.09 ± 0.41°/o	19.99 ± 0.09°/o	99.50 ± 0.80°/o.

Comparison of tables B and C with D and E shows a considerable improvement in the accuracy of the soluble chromium and increased accuracy in all other sections of the analysis. In all subsequent use of synthetic mixtures ε was always less than 0.50°/o for the soluble chromium and around this value for other parts of the analysis. In this, the value of $\varepsilon = 1.23$°/o for insoluble lanthanum

is an exception, although much improved on the figure for the accuracy in table B, and is in fact near the estimated value.

A more general point about synthetic mixtures, and one ignored in the calculation, was the accuracy with which they could be prepared. Great care had to be taken to ensure the minimum uptake of carbon dioxide and moisture by lanthanum (III) oxide when these mixtures were prepared under normal atmospheric conditions.

The calculation below shows how the weight per cent of final products with errors were determined from the experimental parameters. It falls into two parts, an estimation of error in the directly determined quantities, and their use in obtaining the errors in the final products.

Specimen calculation for a reaction in the system La_2O_3-Cr_2O_3

The relative percentage errors for the standardisation ε_{std} were calculated for the sodium thiousulphate used in the titration. The value for both soluble and total soluble chromium was O.31, and that for insoluble chromium was O.24.

For soluble chromium

Weighings

The absolute error for all initial weighings of sample $|d_w|$ had the value $\sqrt{2(0.0002)^2}\,g = 0.0003g$.

This value enabled the calculation of the relative weighing error,

Sample weight	Relative weighing error ε_w
A. O.2165g.	$\frac{O.OOO3}{O.2165} \times 100 = O.14^{o}/o$
B. O.2216g.	$\frac{O.OOO3}{O.2216} \times 100 = O.14^{o}/o$

Titrations

For all titrations less than 50ml. the absolute error d_{tr} = O.O6lml.

Titre	Relative titration error ε_{tr}
A. 33.OOml.	$\frac{O.O61}{33.OO} \times 100 = O.18^{o}/o$
B. 33.82ml.	$\frac{O.O61}{33.82} \times 100 = O.18^{o}/o$

Therefore the total relative error for soluble chromium ε_T is given by:-

$$= \varepsilon_T = \sqrt{(\varepsilon_w)^2 + (\varepsilon_{tr})^2 + (\varepsilon_{std})^2} \text{ where,}$$

$$= \sqrt{(O.14)^2 + (O.18)^2 + (O.31)^2}$$

$$= O.38^{o}/o$$

In a similar way the total relative percentage errors ε_T for the experimentally determinable quantities were calculated and are given in the table below.

Experimental parameter	Weight of sample in grams. A	B	ε_w	ε_{tr}	ε_{ppt}	ε_{std}	ε_T
soluble chromium	O.2156	O.2216	O.14	O.18		O.31	O.38
total soluble chromium	O.3082	O.3077	O.10	O.21		O.31	O.39
insoluble chromium	O.3082	O.3077	O.10	O.14		O.24	O.30
insoluble lanthanum	O.3082	O.3077	O.10		3.57		3.57
soluble lanthanum	O.2941	O.2700	O.11		O.23		O.25

Note: ε_{ppt} refers to the relative error in weighing the precipitated lanthanum oxide. The absolute error in weighing was given by:-

$$d_{ppt} = \sqrt{4(O.OOO2)^2}\ g.$$

$$= O.OOO4g.$$

To be able to calculate errors in the final products the absolute errors in the experimental parameters must be known. These were determined from the results knowing the relative percentage errors ε_T for each of the experimentally determined quantities and are shown in the table below.

Experimental parameter	Results A	B	$\bar{X}$	$\mathcal{E}_T$	Absolute error d °/o
soluble chromium	6.63	6.64	6.64	O.38	O.O25
total soluble chromium	8.47	8.47	8.47	O.39	O.O33
insoluble chromium	12.7O	12.65	12.68	O.3O	O.O38
insoluble lanthanum	3.13	3.O8	3.11	3.57	O.111
soluble lanthanum	52.74	52.8O	52.77	O.25	O.132

It was then possible to calculate the percentage of final products in the reacted analysis sample and their respective errors.

a) Lanthanum chromate (V) and lanthanum chromate (VI)

These final products are related to the experimentally determined quantities in the following way:-

$$\%\text{ by weight } LaCrO_4 = \frac{3}{O.2040}\,[(\text{Total soluble chromium} - \text{soluble chromium})]$$

$$\%\text{ by weight } La_2(CrO_4)_3 = \frac{1}{O.2492}\,[\text{T. sol. chromium} - 3(\text{T. sol. chromium} - \text{soluble chromium})]$$

Their respective absolute errors $|d|$ in the final products are for:

$$LaCrO_4 = \frac{3}{O.2040}\,[\sqrt{(O.O33)^2 + (O.O25)^2}\,] = O.61$$

and

$$La_2(CrO_4)_3 = \frac{1}{O.2492}\,[\sqrt{(O.O33)^2 + (3 \times O.O41)^2}\,] = O.51$$

b) Lanthanum oxide

Unreacted lanthanum oxide was determined from the

appropriate experimental parameters by the formula:-

$$\%\text{ weight } La_2O_3 = \frac{1}{0.8527}\,[\%\text{ wt. soluble lanthanum} - \%\text{ wt. lanthanum in } LaCrO_4 - \%\text{ wt. lanthanum in } La_2(CrO_4)_3]$$

Thus the absolute error in lanthanum oxide is given by:

$$d = \frac{1}{0.8527}\,[\sqrt{(0.132)^2 + (0.61 \times 0.5450)^2 + (0.51 \times 0.4440)^2}]$$

c) Lanthanum chromite

This was determined directly from the insoluble lanthanum determination by multiplying by the ratio of weight of lanthanum chromite to lanthanum in the chromite.

$$\text{Then, } \%\text{ wt. } LaCrO_3 = \frac{1}{0.5815} \times \%\text{ wt. of insoluble lanthanum.}$$

Here the error in the final product was found by multiplying the final percent weight of lanthanum chromite by the relative error of the insoluble lanthanum.

$$\text{Therefore } d = 5.35 \times \frac{3.57}{100} = 0.19\%$$

d) Chromic oxide

The % weight of chromic oxide was determined from the following relationship

$$\%\text{ wt. } Cr_2O_3 = \frac{1}{0.6842}\,(\%\text{ insoluble chromium} - \%\text{ insoluble chromium in lanthanum chromite})$$

The corresponding absolute error is,

$$d = \frac{1}{0.6842}\,[\sqrt{(0.038)^2 + (0.19 \times 0.2176)^2}\,] = 0.08$$

Analysis results with errors

$La_2(CrO_4)_3$	$LaCrO_4$	$LaCrO_3$
11.96 ± 0.51	26.91 ± 0.61	5.35 ± 0.19
La_2O_3	Cr_2O_3	Total
38.46 ± 0.50	16.83 ± 0.08	99.51 ± 0.96

Analysis in the system Y_2O_3-Cr_2O_3

The scheme used and tested for the system La_2O_3-Cr_2O_3 was used with one minor modification. The solubility of yttrium oxide in 2N hydrochloric acid was considerably less than that for lanthanum oxide and those conditions found suitable for the separation of lanthanum (III) oxide from chromite and chromic oxide were not suitable here. To completely dissolve yttrium oxide from a mixture it was found necessary to add the 25ml. hydrochloric acid as before and heat gently, while stirring, for 30 minutes. The solution was then filtered through Whatmans' No. 42 filter paper as previously.

This being a minor proceedural alteration it was not thought necessary to test it using synthetic mixtures.

Analysis in the system Pr_2O_3-Cr_2O_3

Although the analysis scheme can be used as a framework, the difficulties encountered because of the subsequent formation of the higher oxide PrO_x ($1.5 < x < 2.0$) made extensive modification necessary.

It was no longer possible to determine praseodymium

gravimetrically as the oxide since heating in air would give the non-stoichiometric higher oxide. Therefore, it was determined gravimetrically as the oxalate. The oxalate was precipitated as described for the lanthanum oxide - chromic oxide system. It was then filtered onto porosity 3 sintered glass crucibles and washed twice with a dilute oxalic acid solution and once with distilled water. The precipitate was then dried in an oven at 50°C for at least three hours, before weighing the decahydrate [$Pr_2(C_2O_4)_3.10H_2O$].

The praseodymium oxide supplied was black Pr_6O_{11}. It had therefore to be reduced to the (III) oxide Pr_2O_3. This had been done (Sevost'yana, 1965) under a hydrogen stream at 600°C. The conditions used in the present work, and found to be optimum were, heating to a maximum temperature of 800°C, remaining one hour at that temperature and then cooling to room temperature in the hydrogen stream.

For praseodymium (III) oxide, (Pr_2O_3) % praseodymium

Calc.	Found
85.45	85.52.

There remained two major problems of analysis in this system:

1) Could the extent of oxidation of the (III) oxide be determined, i.e. the value of x in PrO_x where $1.5 < x < 2.00$.

2) Further, was it possible to accurately determine soluble chromium in the presence of this higher oxide. This problem

arose because PrO_x is partially soluble in 2N. hydrochloric acid and praseodymium (IV), a very powerful oxidising agent, would oxidise chromium (III) from the disproportionation of praseodymium chromate (V), if present, to chromium (VI).

In order to dissolve all the PrO_x 5ml. of concentrated hydrochloric acid were added and after 5 minutes diluted to 25ml.

The solvolytic disproportionation of PrO_x has been reported using water (Brauer, 1963) and with acetic acid of varying strengths (Clifford, 1963) and by others. In the case of the hydrolytic process, it was said to be essentially complete after 1h, whereas those methods using acetic acid took several days. The hydrolytic process was represented by the equation:-

$$PrO_x + (6-3x)H_2O \rightarrow (4-2x)\ Pr(OH)_3 + (2x-3)\ PrO_2.$$

Therefore it was essential to find a satisfactory means of separating the praseodymium hydroxide from the dioxide.

Brauer's method of refluxing for 10 minutes with a 90% solution of acetic acid proved too severe as it also dissolved, in addition to the hydroxide, significant amounts of the dioxide. Optimum conditions for the separation of hydroxide and dioxide by solution of the former were hydrolytic disproportionation involving reflux for two hours followed by, when cooled, the addition of 50ml. glacial acetic acid to the 5ml. of water already present, and stirring overnight.

Praseodymium chromate (V), which dissolves with greater

difficulty than the corresponding chromate (VI), was found to dissolve overnight in a solution of 5ml. water and 50ml. acetic acid. It then became possible to combine the determination of soluble chromium with that for oxidised praseodymium, Pr(IV), as part of an analysis scheme.

Two sets of determinations remained fundamentally unaltered, those in which total soluble chromium is determined and that in which soluble praseodymium, insoluble chromium, and insoluble praseodymium are determined; but here soluble praseodymium was dissolved out by adding 5ml. concentrated hydrochloric acid and then diluting to 25ml. with distilled water.

Sample weights of approximately 0.30g. were used to analyse for soluble chromium and praseodymium (IV). To this amount of reacted sample were added 5ml. of distilled water, and the mixture was refluxed for two hours. When cooled, 50ml. acetic acid were added and the mixture was stirred for periods between 16-24h. The solid was filtered onto a porosity 4 sintered glass crucible.

To the solid generally containing in addition to praseodymium dioxide, chromite and chromic oxide, were added 6ml. concentrated hydrochloric acid to dissolve the dioxide. Then after 5 minutes the solution containing Pr(IV) was diluted to 30ml., subsequently to 200ml., and boiled for about 30 minutes until the volume of the solution was about 50ml. This was then filtered through Whatmans' No. 42 filter

papers to remove chromic oxide and praseodymium chromite. The solution containing praseodymium was again diluted to approximately 200ml. and the praseodymium oxalate decahydrate precipitated by adding hot oxalic solution dropwise, and then weighed after drying to give the percentage oxidised praseodymium present [Pr(IV)].

Soluble chromium dissolved in the acetic acid solution was determined by adding approximately 2g. potassium iodide and titrating with approximately O.O25N sodium thiosulphate solution.

To test the analysis outlined above a synthetic mixture containing by weight 25.36°/o praseodymium chromate (V), 39.55°/o black praseodymium oxide (Pr_6O_{11}) and 35.09°/o chromic oxide was prepared. The results of the analysis are given below in table F.

TABLE F Analysis of a synthetic mixture containing praseodymium chromate (V), praseodymium oxide (Pr_6O_{11}) and chromic oxide.

	Results				Accuracy °/o		Precision °/o	
	A	B	$\bar{X}$	Calc.	εact.	εest.	δ	$\delta/\bar{X}$
Soluble chromium	3.51	3.51	3.51	3.49	.57	.58	.00	00
Total soluble Cr	5.04	5.04	5.04	5.04	00	.60	.00	00
Insoluble chromium	24.03	24.06	24.05	24.01	.17	.36	.03	.08
Soluble praseodymium	48.84	46.97	46.93	46.98	.11	.13	.04	.09
Oxidised Pr (PrO_2)	21.85	21.98	21.92	21.91	.05	.47	.07	.27

The analysis results give:-

$PrCrO_4$	Pr_6O_{11}	Cr_2O_3	Total
25.04 ± 0.59%	39.71 ± 0.20%	35.17 ± 0.13%	99.91 ± 0.64%

(N.B. For the purposes of the calculation the value of x for the praseodymium oxide was taken to be 1.833).

From the analysis we can obtain a value for praseodymium (IV), and also determine the soluble praseodymium, which contains praseodymium (IV) and (III) from the oxide, and praseodymium from the chromate. The value of x, giving the extent of oxidation of the oxide is found from the formula:-

$$x = \left[\frac{1}{2}\left(\frac{\%\text{ wt. Pr(IV)}}{\%\text{ soluble Pr} - \%\text{ praseodymium in chromate}}\right)\right] + 1.50$$

The percentage formation of chromate was obtained from the soluble and total soluble chromium, and from these were obtained the praseodymium content of the chromate, and by subtraction, the soluble praseodymium arising only from the oxide was determined.

In the final determination of products the percentage weight of PrO_x in the sample was given by:-

$$\%\text{ weight of } PrO_x = \%\text{ soluble praseodymium (oxide only)} \times \frac{\text{molecular weight } PrO_x}{\text{Atomic Wt. Pr}}$$

Preparation of samples for reaction

The lanthanum oxide used was ultra pure as supplied by Alfa Inorganics Ventron U.S.A., while the yttrium oxide was 99.99% pure B.D.H. laboratory reagent. The praseodymium oxide was supplied 99.99% pure as B.D.H. laboratory reagent Pr_6O_{11} and the

chromic oxide used was B.D.H. laboratory reagent of purity not less than 98.99°/o.

It was necessary, as far as possible, to standardise the thermal pretreatment of reactants; also, to ensure an intimately ground and stoichiometrically uniform mixture, a standard procedure of preparation was adopted.

Lanthanum oxide, approximately 10g., was sintered at around 900°C in air using a full meker flame and initially mixed with the stoichiometric quantity of chromic oxide previously calcined under the same conditions. After initial mixing was complete the mixture was split up into batches of approximately 4g., then, each batch was ground and mixed for ten minutes with an agate mortar and pestle before a final mixing of all the mixture.

The yttrium oxide - chromic oxide mixture was made up under the same conditions as used for lanthanum oxide.

It was not possible to sinter the praseodymium (III) oxide produced by reduction, and this was mixed with sintered chromic oxide in the manner previously described.

The mixture was pelleted for reaction using a Perkin-Elmer 13mm dye by adding approximately 1g. of mixture, and applying a pressure of 10t/sq.in. Pellets were used merely for consistency, as preliminary reactions using powders showed little difference in nature and extent of reaction from those, in which latterly, pellets were used. Thus this macroscopic stage in the preparation of samples

is relatively unimportant in affecting the reaction.

The polymorphism of La_2O_3, Y_2O_3 and Pr_2O_3

It was necessary to determine the crystalline modification of each of the lanthanide oxides as present in the reaction mixtures.

Comparison of x-ray powder diffraction d-spacings of the three possible crystalline modifications with that obtained from La_2O_3 sintered under the conditions used in the preparation of the reaction mixture showed that its structure was that of the A-type (hexagonal) form of the lanthanum (III) oxide. At the temperatures of reaction this is the only stable form of the oxide (Roth and Schneider, 1960).

Yttrium oxide calcined under the conditions used in the pretreatment of the oxide before inclusion in the reaction mixture displayed only the lines of the C-type (cubic) oxide. The C-type form would be expected to be the only stable form according to Roth and Schneider (1960).

The praseodymium (III) oxide was shown to have the A-type (hexagonal) structure after the reduction from Pr_6O_{11}, under the conditions previously described for the preparation of the praseodymium (III) oxide. The A-type Pr_2O_3 is only stable in the absence of oxygen, at the temperatures of reaction studied, because of the oxidation to higher oxides PrO_x $1.5 < x < 2.00$, which have different structures.

RESULTS SECTION

(1) The La_2O_3-Cr_2O_3 system

Series of reactions were analysed as described. They were of two distinct types, either isothermal at differing times or isochronous for a range of temperatures.

Isothermals were carried out between 560-640°C. The temperature dependence characteristics were examined for periods of 32 hours in air, for the range of temperatures 300-700°C, for periods of 8 hours between 560-740°C in oxygen, and in the range 600-1000°C for periods of 4 hours in argon. In addition, a direct comparison of the effect of oxygen and air atmospheres was made for times of 4 hours in the range of temperatures 580-640°C.

Isothermals at 560°C, 580°C, 590°C, 600°C, 620°C, 640°C

The results at each temperature expressed as weight per cent product are given in tables 1 - 6 and the plots of per cent by weight product formed against time are given in figures 1 - 6. The total product, which is the sum of the yields of the individual products was also plotted for each temperature against time.

Three products were obtained from the reactions carried out isothermally at temperatures between 560 - 640°C in the reaction period 0-32 hours. These were, lanthanum chromate (VI), present at all temperatures and times, lanthanum chromate (V) and lanthanum chromite : generally, lanthanum chromate (V) was present at lower temperatures and shorter reaction times and ~~lanthanum~~

TABLE 1 Results of 560°C. isothermal O-32 hours.

Time	$La_2(CrO_4)_3$	$LaCrO_4$	$LaCrO_3$	La_2O_3	Cr_2O_3	Total
1hr.	3.37	7.79	-	59.74	28.14	99.04
2hr.	5.86	10.88	-	56.09	26.19	99.02
4hr.	7.83	15.29	-	52.14	23.82	99.08
8hr.	10.43	20.00	-	46.16	21.12	97.71
16hr.	11.56	28.97	-	40.51	17.80	98.84
32hr.	11.24	41.03	-	32.65	14.35	99.27

TABLE 2 Results of 580°C. isothermal O-32 hours.

Time	$La_2(CrO_4)_3$	$LaCrO_4$	$LaCrO_3$	La_2O_3	Cr_2O_3	Total
1hr.	3.65	8.97	-	58.66	27.70	98.98
2hr.	9.79	13.82	-	51.46	23.25	98.32
4hr.	10.59	24.85	-	43.53	19.56	98.53
8hr.	12.14	31.76	-	37.83	16.73	98.76
16hr.	13.24	37.06	5.30	30.51	12.94	99.02
24hr.	13.32	25.74	22.61	26.96	11.46	100.09
32hr.	11.96	6.91	47.84	21.91	9.72	98.34

TABLE 3 Results of 590°C. isothermal O-32 hours.

Time	$La_2(CrO_4)_3$	$LaCrO_4$	$LaCrO_3$	La_2O_3	Cr_2O_3	Total
1hr.	5.74	11.03	-	56.10	25.91	98.78
2hr.	7.74	16.03	-	51.60	23.62	98.99
4hr.	9.47	22.50	0.91	45.69	20.65	99.22
8hr.	11.96	26.91	5.35	38.46	16.83	99.51
16hr.	10.51	7.06	39.36	29.33	13.04	99.30
32hr.	11.88	-	52.84	23.99	10.54	98.25

TABLE 4 Results of 600°C. isothermal O-32 hours.

Time	$La_2(CrO_4)_3$	$LaCrO_4$	$LaCrO_3$	La_2O_3	Cr_2O_3	Total
1hr.	8.51	12.35	-	53.07	24.47	98.40
2hr.	10.35	19.12	-	47.21	21.53	98.21
4hr.	11.08	27.35	2.17	40.40	18.08	99.08
8hr.	11.20	11.76	32.31	29.89	13.68	98.84
16hr.	11.24	-	53.84	22.94	10.62	98.64
32hr.	11.80	-	60.17	18.62	8.47	99.06

TABLE 5 Results of 620°C. isothermal O-32 hours.

Time	$La_2(CrO_4)_3$	$LaCrO_4$	$LaCrO_3$	La_2O_3	Cr_2O_3	Total
1hr.	10.63	14.85	2.55	48.90	22.28	99.21
2hr.	13.24	7.79	16.63	44.15	18.62	100.43
4hr.	13.40	-	33.38	37.75	15.88	100.41
8hr.	15.21	-	39.47	31.39	13.46	99.53
16hr.	15.85	-	47.96	25.48	10.60	99.89
32hr.	14.73	-	56.78	19.87	8.13	99.51

TABLE 6 Results of 640°C. isothermal O-32 hours.

Time	$La_2(CrO_4)_3$	$LaCrO_4$	$LaCrO_3$	La_2O_3	Cr_2O_3	Total
1hr.	13.20	3.68	22.75	40.62	18.47	98.72
2hr.	14.09	-	37.18	33.57	15.04	99.88
4hr.	15.45	-	43.87	28.38	12.13	99.33
8hr.	14.93	-	53.55	21.55	9.10	99.13
16hr.	11.52	-	68.94	13.31	5.86	99.63
32hr.	9.03	-	79.04	8.77	3.36	100.20

lanthanum chromite at higher temperatures and longer reaction times.

Throughout these reactions, in the absence of appreciable amounts of the chromite, i.e. less than 2%, lanthanum chromate (V) was present in larger amounts than lanthanum chromate (VI). When there was no chromate (V) present the amount of lanthanum chromite formed was always greater than the amount of chromate (VI). In the presence of both lanthanum chromate (V) and lanthanum chromite, they could either be less than or greater than each other and lanthanum chromate (VI), depending on temperature and time.

The rate of formation of lanthanum chromate (VI) and lanthanum chromate (V) decreased with increasing time. This was most salient for lanthanum chromate (VI), the rate of formation decreased markedly between 1 - 8 hours, in the range 560-590°C, and 1 - 4 hours, at 600°C; and was, within experimental error, constant from 8 - 32 hours in the range 560-590°C, and from 4 - 32 hours at 600°C, but at 620°C and 640°C although showing the same behaviour, the stationary period had a more definite maximum. The rate of formation of lanthanum chromite, between 580-620°C, increased with time for at least part of the reaction period; while at 640°C no acceleratory period in the formation of lanthanum chromite was observed.

The rate of formation of chromate (VI) in the interval 0 - 4 hours increased from 560-640°C, with the exception of 590°C which was out of sequence between 580°C and 600°C in this

respect, the greatest effect being observed within the first hour of reaction. In the period 4 - 32 hours the effect of temperature was much less marked but at 620°C and 640°C the comparatively flat region of the curve occurred around 15°/o which was 2 or 3 per cent higher than in the range 560-600°C.

There was no significant decrease in the amount of lanthanum chromate (VI) until 16 hours reaction at 620°C, where the chromate (VI) had reached a maximum value of 15.85°/o,which amount decreased by approximately 1°/o in the interval 16 - 32 hours. At 640°C, however, the maximum of chromate (VI) formation occurred at 4 hours reaction time. A decrease of less than 1°/o between 4 - 8 hours was followed by a significant decrease of 3.41°/o, between 8 - 16 hours, and 2.49°/o from 16 - 32 hours.

No substantial decrease in the amount of lanthanum chromate (V) at 560°C was observed, but a decrease did occur at 580°C after 16 hours reaction, where chromate (V) had reached a maximum value of 37.06°/o. Thereafter the lanthanum chromate (V) showed progressively faster formation and decomposition as temperatures increased, thus the maxima appeared at successively shorter time intervals each generally exhibiting a decrease in chromate (V) from that formed at lower temperatures. Thus at 640°C the only chromate (V) present was 3.68°/o after one hours' reaction time. The behaviour at 590°C was again slightly anomalous for the maximum was lower than at 580°C, (figure 7).

The rate of decomposition of the chromate (V) increased with time over the greater part of the total decomposition period, which decreased as the temperature was raised from over 16 hours at 580°C to under 3 hours at 620°C.

Lanthanum chromite, unlike lanthanum chromate (V) and lanthanum chromate (VI) showed no rapid initial formation except at 640°C. In the temperature range 580-620°C formation of significant amounts of chromite (more than 2%) began with an increase in rate with time. With increasing temperature this commenced at decreasing reaction times and lasted for successively shorter periods. Thus at 580°C the accelerated increase took place between 8 - 32 hours, at 590°C 4 - 16 hours, at 600°C 2 - 8 hours, while at 640°C no acceleration in the formation of chromite was observed. These periods and temperatures correlate with the decomposition of lanthanum chromate (V); also, the maximum value of chromate (V) coincides with the first appearance of amounts of chromite greater than 2%. Excepting 580°C, the period 16 - 32 hours was markedly a period of decrease in the rate of lanthanum chromite formation. The amount of chromite formed in this period diminished from 580°C to 600°C, but increased slightly from 600-620°C and 620-640°C. It was at 620°C and 640°C, in the period 16 - 32 hours, that chromate (VI) began to decrease and this is no doubt a contributory factor in the increase in the amount of chromite, (figure 8).

The total product, when plotted for each temperature

against time gave a smooth curve with the rate continuously decreasing with time (figure 9). From this it could be seen that a plot of percentage weight of (lanthanum chromate (V) + lanthanum chromite) as shown for the isothermal at 590°C (figure 10) would also give a curve with the same characteristics. The total product displays a rapid relative rate of increase with temperature in the interval 0 - 8 hours, and the ratio of the total product formed after 2 hours to that formed after 32 hours increases with temperature. The period 8 - 32 hours, however, shows appreciable decrease in rate, and in the period 16 - 32 hours for all temperatures except 560°C, the total product increased approximately 6-8°/o.

Temperature dependence in the range 300-700°C at periods of 32 hours in air.

Table 7 gives the results obtained from reaction in air for a period of 32 hours in the range 300-700°C, and figure 13 presents those results graphically for the range 400-700°C.

In this temperature range three products were determined, lanthanum chromate (VI) from 350°C-700°C, lanthanum chromate (V) from 420-580°C and lanthanum chromite in the range 580-700°C.

At 350°C, where the first product was detected until 560°C lanthanum chromate (VI) increased steadily, to a maximum, at 620°C; after this temperature, the chromate (VI) decreased, falling more than 5°/o between 620-640°C, and continued to drop until at 700°C, 1.57°/o remained with almost 100°/o total product.

TABLE 7 Results of reactions in the temperature range 300-700°C. in air for 32 hours.

Temp.	$La_2(CrO_4)_3$	$LaCrO_4$	$LaCrO_3$	La_2O_3	Cr_2O_3	Total
300°C	(0.24)*	-	-	66.91	31.58	98.73
350°C	0.64	-	-	66.83	31.61	99.08
400°C	3.57	-	-	65.35	30.18	99.10
420°C	4.25	2.06	-	63.93	29.04	99.28
440°C	3.97	3.82	-	62.28	28.79	98.86
460°C	4.05	7.79	-	59.65	27.55	99.04
480°C	5.06	11.18	-	56.93	26.26	99.43
500°C	6.42	15.88	-	53.20	24.25	99.75
520°C	7.54	20.29	-	49.67	22.42	99.92
540°C	9.43	27.94	-	43.81	19.19	100.33
560°C	11.24	41.03	-	32.65	14.35	99.27
580°C	11.96	6.91	47.84	21.91	9.72	98.34
590°C	11.88	-	52.84	23.99	10.54	98.99
600°C	12.80	-	56.82	20.92	8.91	99.45
610°C	13.84	-	58.45	19.50	8.07	99.86
620°C	14.73	-	56.78	19.87	8.13	99.66
640°C	9.55	-	77.39	9.79	3.74	100.47
660°C	4.86	-	91.18	3.33	1.01	100.38
700°C	1.57	-	98.23	-	0.12	99.92

* The amount of chromate denoted thus ( )* is not significant.

Lanthanum chromate (V) exhibited an increase in the rate of formation from 420°C, at which temperature the first significant amounts were analysed, to 560°C, where the maximum of 41.03°/o was obtained. At 580°C chromate (V) had decreased to 6.91°/o with none remaining at 590°C.

No lanthanum chromite was detected below 560°C, but between 560-580°C it formed very rapidly, with 48°/o present at 580°C; and, in the temperature range 580-610°C a further increase of approximately 10°/o was observed. A maximum of chromite formation occurred at 610°C, because of a slight decrease in product at 620°C, but chromite formation increased rapidly; though with a decrease in rate between 620°C and 660°C and a more marked decrease in rate from 660-700°C.

The increase in chromite from 620-670°C coincided with the commencement of lanthanum chromate (VI) decomposition, although the decrease in chromate (VI) would not appear to account for all the chromite formed. The initial increase in chromite occurred in the same range as the decomposition of lanthanum chromate (V), and here it was possible that between 560-600°C all the chromite could result from chromate (V) decomposition. A plot of the combined products of lanthanum chromate (V) and lanthanum chromite against temperature gives, within experimental error, a smooth continuous curve from 500-610°C, figure 12, with a point of inflexion at 560°C, showing accelerated formation below this temperature, and decay above.

Temperature dependence in the range 600-975°C for times of 4 hours in argon.

Reactions in argon permitted the study of the La_2O_3-Cr_2O_3 system without the interference of mechanisms involving chromate formation or decomposition. The shape of curve obtained was much simpler (figure 14). The results are given in table 8, as per cent weight.

TABLE 8 Results of temperature dependence in an Argon atmosphere.

Temp.	$La_2(CrO_4)_3$	$LaCrO_4$	$LaCrO_3$	La_2O_3	Cr_2O_3	Total
600°C	-	-	4.45	64.55	29.99	98.09
650°C	-	-	6.17	63.90	29.83	99.90
700°C	-	-	13.93	58.51	27.26	99.70
750°C	-	-	18.80	54.79	25.87	99.46
800°C	-	-	27.60	48.98	23.06	99.64
850°C	-	-	32.79	45.29	21.42	99.50
900°C	-	-	33.76	44.54	21.04	99.34
950°C	-	-	33.12	45.12	21.27	99.51
975°C	-	-	33.72	44.45	21.09	99.26

Only one product was obtained, lanthanum chromite. The chromite increased slowly, with a slight acceleration, from 4.4% at 600°C to 27.60 at 800°C. From 800-975°C a marked decrease in rate with temperature was evident.

Temperature dependence in the range 560-740°C for times of 8 hours in an oxygen flow.

Table 9 gives the analysis results of reactions carried out

TABLE 9 Results of variation of product in the range 560-740°C. in oxygen flow for times of 8 hours.

Temp.	$La_2(CrO_4)_3$	$LaCrO_4$	$LaCrO_3$	La_2O_3	Cr_2O_3	Total
560°C	8.39	9.85	0.89	56.38	25.27	100.78
580°C	12.00	17.79	-	48.71	21.44	99.44
600°C	15.21	21.18	-	43.37	18.91	98.67
620°C	17.38	26.32	1.00	39.73	16.00	100.43
640°C	19.26	17.06	15.20	34.69	13.87	100.08
660°C	20.72	-	38.01	29.76	12.13	100.12
670°C	19.38	-	42.49	27.17	10.87	99.91
680°C	21.19	-	41.13	27.21	10.35	99.88
700°C	17.42	-	55.55	19.74	7.36	100.07
720°C	11.84	-	73.24	10.95	3.94	99.97
740°C	3.43	-	91.83	2.94	2.09	100.79

in this temperature range for 8 hours in an atmosphere of oxygen. The per cent of weight for each product and their sum were plotted against temperature as in figure 15.

The results display many points of similarity to those results obtained in air for periods of 32 hours. Lanthanum chromate (VI) was present throughout the whole temperature range; lanthanum chromate (V) from 560-640°C and lanthanum chromite between 640-740°C.

From 560-640°C a steady increase in the amount of lanthanum chromate (VI) occurred, but in the range 640-680°C the rate of increase was, within experimental error, zero. The maximum chromate (VI) formation was obtained at 680°C, but after this temperature the amount decreased, with a rate which increased with temperature, from 680-740°C.

Lanthanum chromate (V) formation reached a maximum at 620°C and thereafter it decreased with a rate increasing with rise in temperature to zero at 660°C.

The chromite formed only in amounts of 1% or less between 560 and 620°C, but its rate of formation increased with temperature from 620-660°C. The rate of formation slowed considerably from 660 to 670°C, and a slight drop in product at 680°C was followed by a rapid acceleratory increase in chromite formation, with a rate of increase marginally slower than that between 620-660°C.

It can be seen that the temperature range in which lanthanum chromate (V) decomposes corresponds to the range of the initial

increase in chromite, and that the second major increase in chromite occurs during the period of chromate (VI) decrease.

There were several differences between previous isothermals in air, the temperature dependence in air at 32 hours, and the present temperature dependence in oxygen, which may have been attributable to the difference in atmosphere, but may have had another cause. The two most salient differences were a decrease in general reactivity and the decreased ratio of chromate (V) to chromate (VI).

Although small changes in reactivity can occur from one reaction mixture to another, the change here was of a different order and markedly affected the nature and extent of reaction. The change in colour of the reaction mixture, for those reactions in oxygen, prepared from a new supply of chromic oxide, indicated a change in the physical properties of the chromic oxide, e.g. an altered average particle size. A few miscellaneous reactions were undertaken in both air and oxygen to check the likelier factor, whose results are given below.

Isothermal at 560°C in oxygen for times 1hr., 2hr., 4hr. and 8hr.

Time	$La_2(CrO_4)_3$	$LaCrO_4$	$LaCrO_3$	La_2O_3	Cr_2O_3	Total
1hr.	3.53	1.47	-	64.66	29.96	99.62
2hr.	6.02	1.91	1.93	60.60	28.22	98.68
4hr.	6.34	4.85	0.96	60.24	27.52	99.91
8hr.	8.39	9.85	0.89	56.38	25.27	100.78

Reaction at 560°C for 4 hours in air.

$La_2(CrO_4)_3$	$LaCrO_4$	$LaCrO_3$	La_2O_3	Cr_2O_3	Total
8.19	5.15	0.76	59.16	26.77	100.03

Isothermal at 620°C in air for times of 2hr., 4hr. and 8hr.

Time	$La_2(CrO_4)_3$	$LaCrO_4$	$LaCrO_3$	La_2O_3	Cr_2O_3	Total
2hr.	11.20	7.79	1.05	55.15	24.67	99.86
4hr.	14.17	12.79	-	49.54	22.03	98.53
8hr.	15.21	21.18	-	43.37	18.91	98.67

Comparison of the results above with those in air at 560°C and 620°C, in tables 1 and 5, showed that the reactivity had changed with the change in mixture in the way described. The effect of an oxygen atmosphere remained, however, more ambiguous. Therefore to compare the effect of an oxygen atmosphere with that of air, reactions in a flow of air and oxygen in the temperature range 580-640°C were analysed, using the same mixture, under otherwise identical conditions of reaction.

Comparison of reaction in air and oxygen atmospheres for times of 4 hours at 580°C, 600°C, 620°C and 640°C.

The results are given in table 10, and shown graphically in figure 16. They show a total product in oxygen which is always greater than that in air by 6-8%, although, lanthanum chromate (VI), lanthanum chromate (V) and lanthanum chromite, which constituted the total, showed a considerable variation with atmosphere and temperature.

TABLE 10 Results of a comparison of air and oxygen atmospheres for times of 4 hours at temperatures 580°C, 600°C, 620°C and 640°C.

Atmos.	Temp.	$La_2(CrO_4)_3$	$LaCrO_4$	$LaCrO_3$	La_2O_3	Cr_2O_3	Total
Air	580°C	9.83	6.17	1.58	56.24	25.34	99.16
O_2	580°C	9.27	16.47	-	50.95	22.93	99.62
Air	600°C	14.61	9.26	5.16	49.19	21.58	99.80
O_2	600°C	10.83	24.85	0.69	43.20	19.59	99.16
Air	620°C	17.90	0.74	17.90	44.52	18.86	99.92
O_2	620°C	13.12	26.47	0.79	41.53	18.02	99.93
Air	640°C	22.87	-	17.49	43.00	17.09	100.45
O_2	640°C	16.01	18.97	11.04	38.52	16.06	100.60

At the temperatures studied lanthanum chromate (VI) formed in slightly greater amount in air than in oxygen, with a faster rate of formation in air, from 1°/o greater in amount at 580°C to 7.5°/o at 640°C.

However, lanthanum chromate (V) was present in considerably higher yield in oxygen than in air and began decomposition at a higher temperature in oxygen, 620°C, as against 600°C in air. The rate of decrease of chromate (V) in both atmospheres after these respective temperatures was approximately equal.

Lanthanum chromite, in this temperature range, formed in larger quantity in air than in oxygen. A yield of chromite, greater than 2°/o, was obtained at 600°C in air, whereas significant amounts of chromite did not form in oxygen until temperatures above 620°C; again coinciding with the decrease in chromate (V). Those small amounts of chromite present before decomposition of the chromate (V) were also greater in air than oxygen.

The initial rates of increase of chromite in both atmospheres, like the initial rates of decrease of chromate (V) in air and oxygen were approximately equal. The rate of formation of chromite, however, showed marked deceleratory behaviour in air before oxygen.

The reaction in which chromate (VI) formed was slower in oxygen, than in air, but this may be due to competition from the more dominant, in oxygen, chromate (V) forming reaction. The above is yet more evidence that two distinct and separate processes are

involved in formation of the different chromates.

Investigation of chromate formation from chromite at lower temperatures.

A 'low temperature' preparation of lanthanum chromite by heating a stoichiometric mixture of the oxides at 690°C for 24 hours with regrinding every 2 hours was undertaken in an attempt to obtain a chromite of poor crystallinity and hence of greater reactivity. It was, under appropriate conditions, heated to examine if the formation of chromate was possible in an oxygen containing atmosphere.

The chromite used was not obtained 100% pure, but contained 1.08% lanthanum chromate (VI) and 99.07% lanthanum chromite, from analysis.

The table below gives the analysis results after heating the chromite under the conditions stated.

Temp.	Time	Atmos.	$La_2(CrO_4)_3$	$LaCrO_4$	$LaCrO_3$	La_2O_3	Cr_2O_3	Total
620°C	4hr.	O_2	1.44	-	97.15	-	0.28	98.87
600°C	24hr.	Air	1.28	-	98.66	-	-	99.94
580°C	8hr.	O_2	1.65	-	97.88	-	-	99.53
600°C	8hr.	O_2	1.61	-	97.76	-	0.01	99.38

Within experimental error, no significant oxidation of chromite took place. Therefore formation of chromate was not possible from chromite at these temperatures.

FIGURE 1

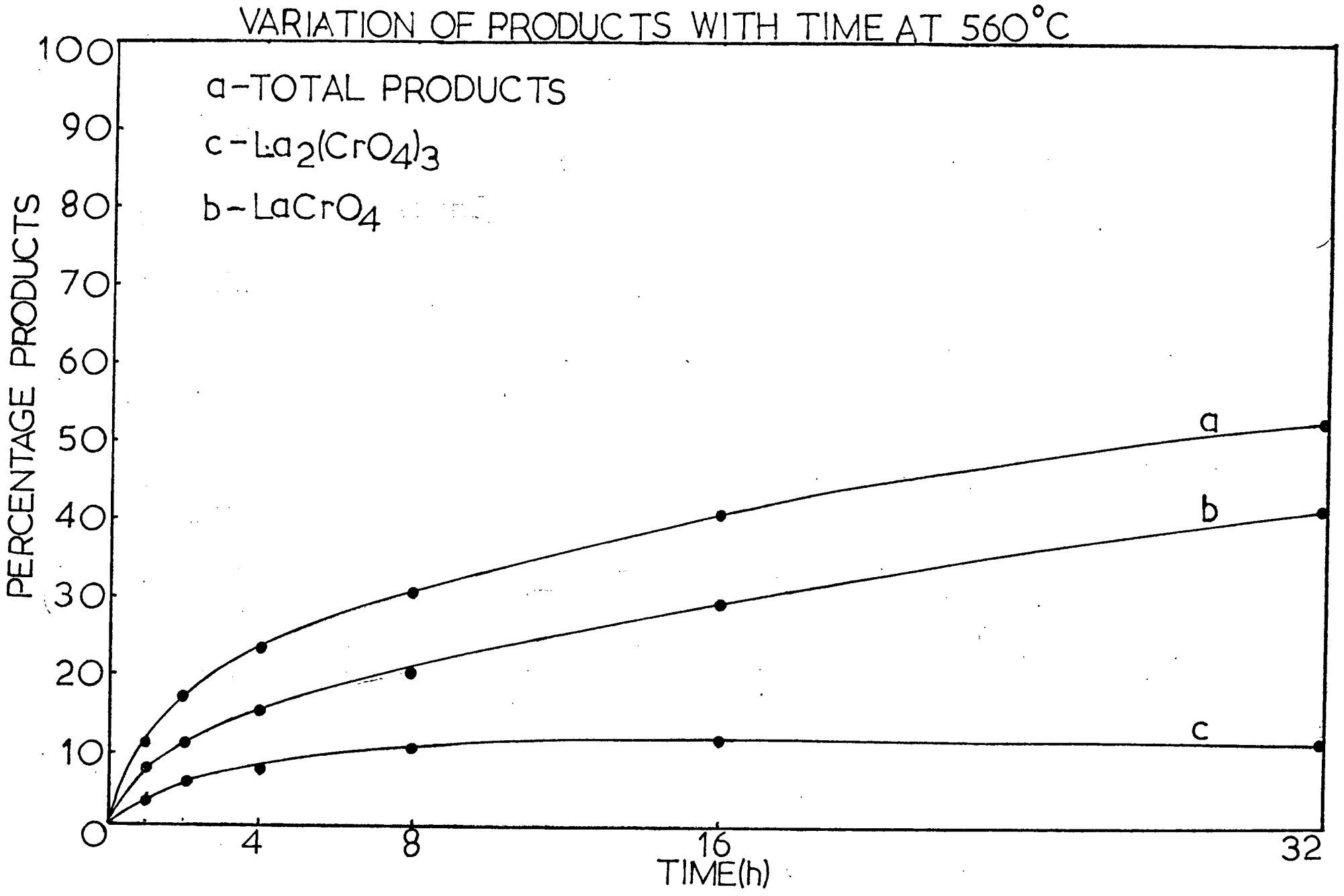

VARIATION OF PRODUCTS WITH TIME AT 560°C
a-TOTAL PRODUCTS
c-La2(CrO4)3
b-LaCrO4
PERCENTAGE PRODUCTS
100
90
80
70
60
50
40
30
20
10
0
4
8
16
32
TIME(h)
a
b
c

FIGURE 2

VARIATION OF PRODUCTS WITH TIME AT 580°C

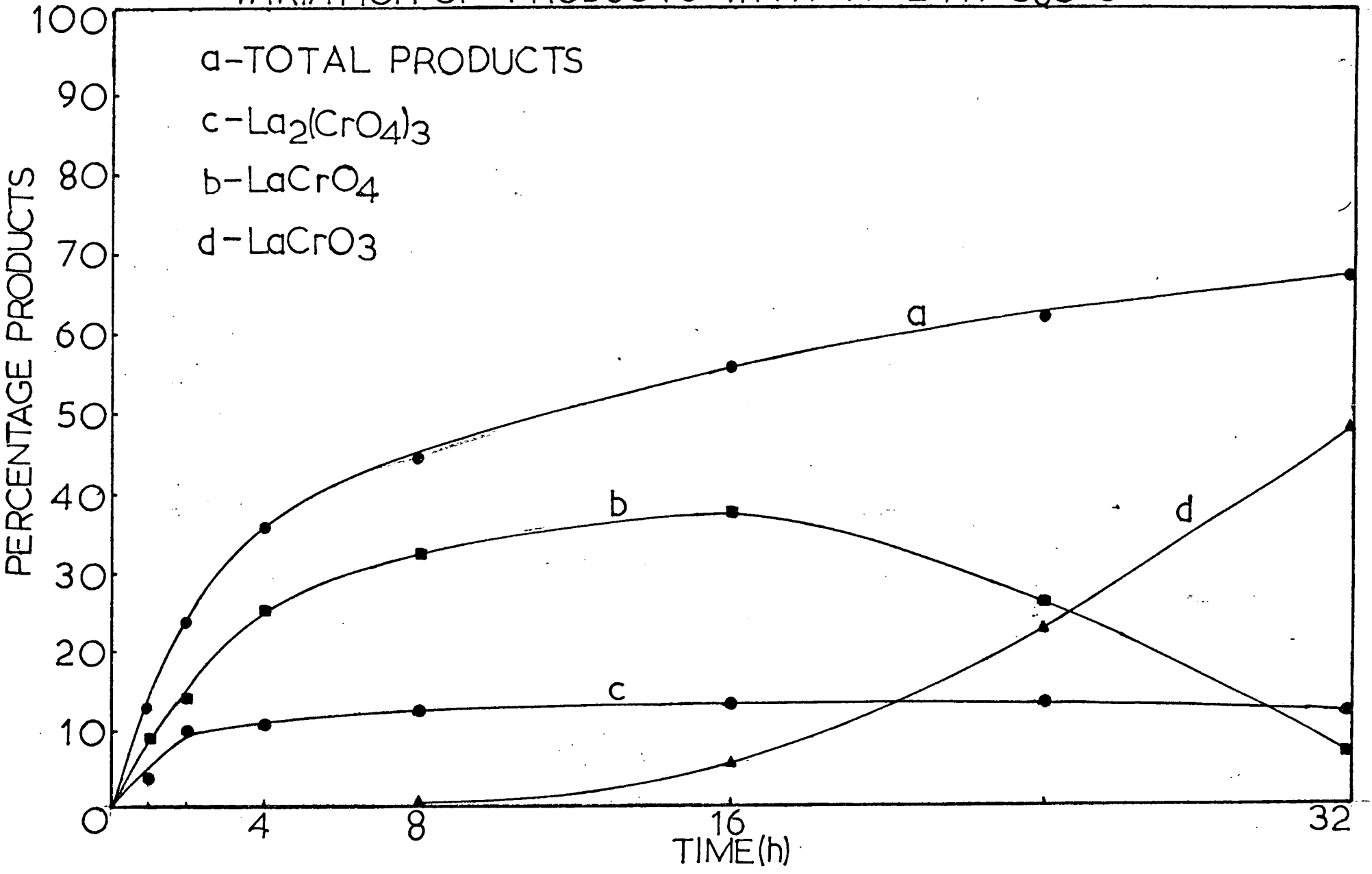


FIGURE 3

VARIATION OF PRODUCTS WITH TIME AT 590 °C

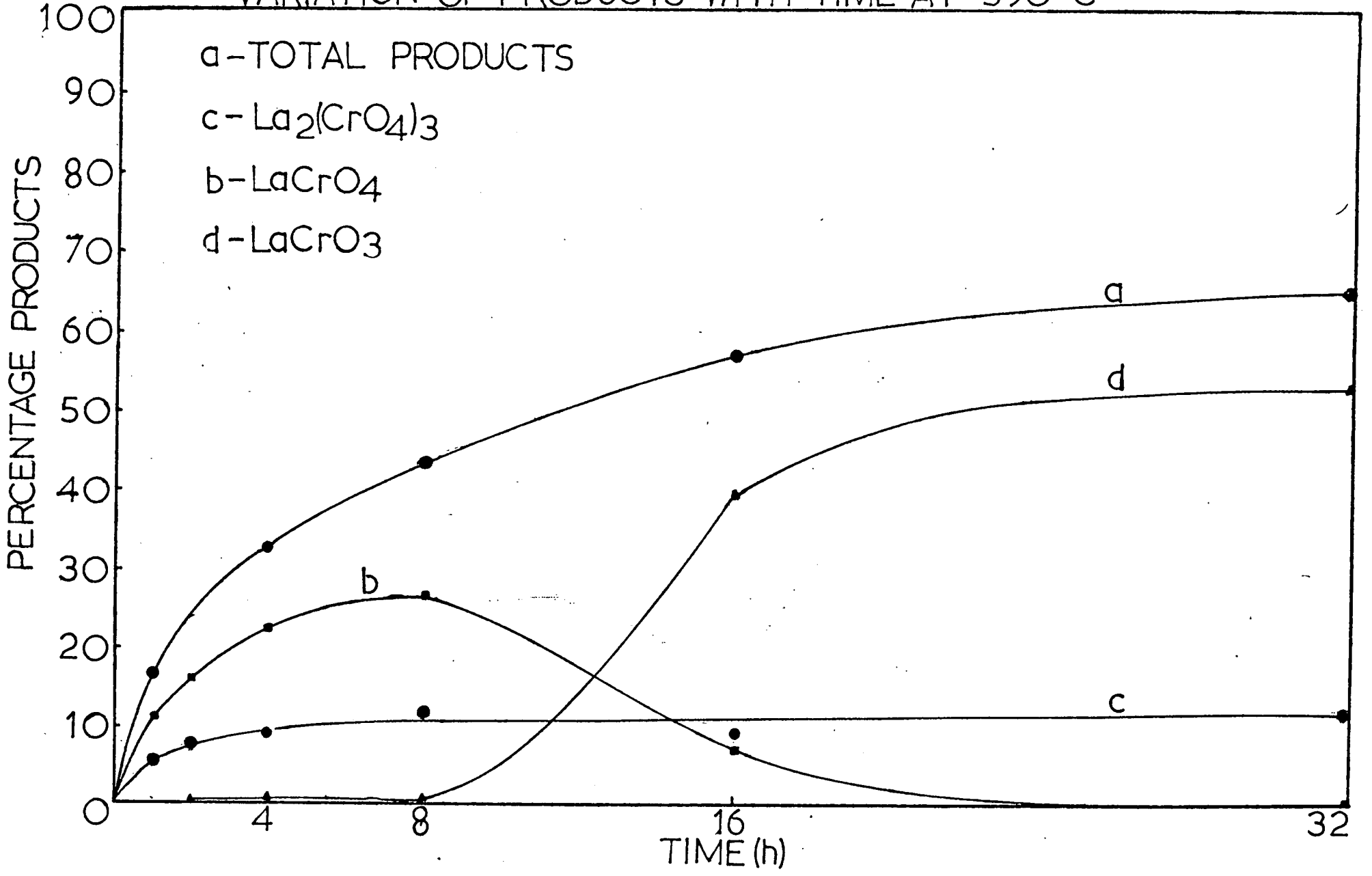


FIGURE 4

VARIATION OF PRODUCTS WITH TIME AT 600°C

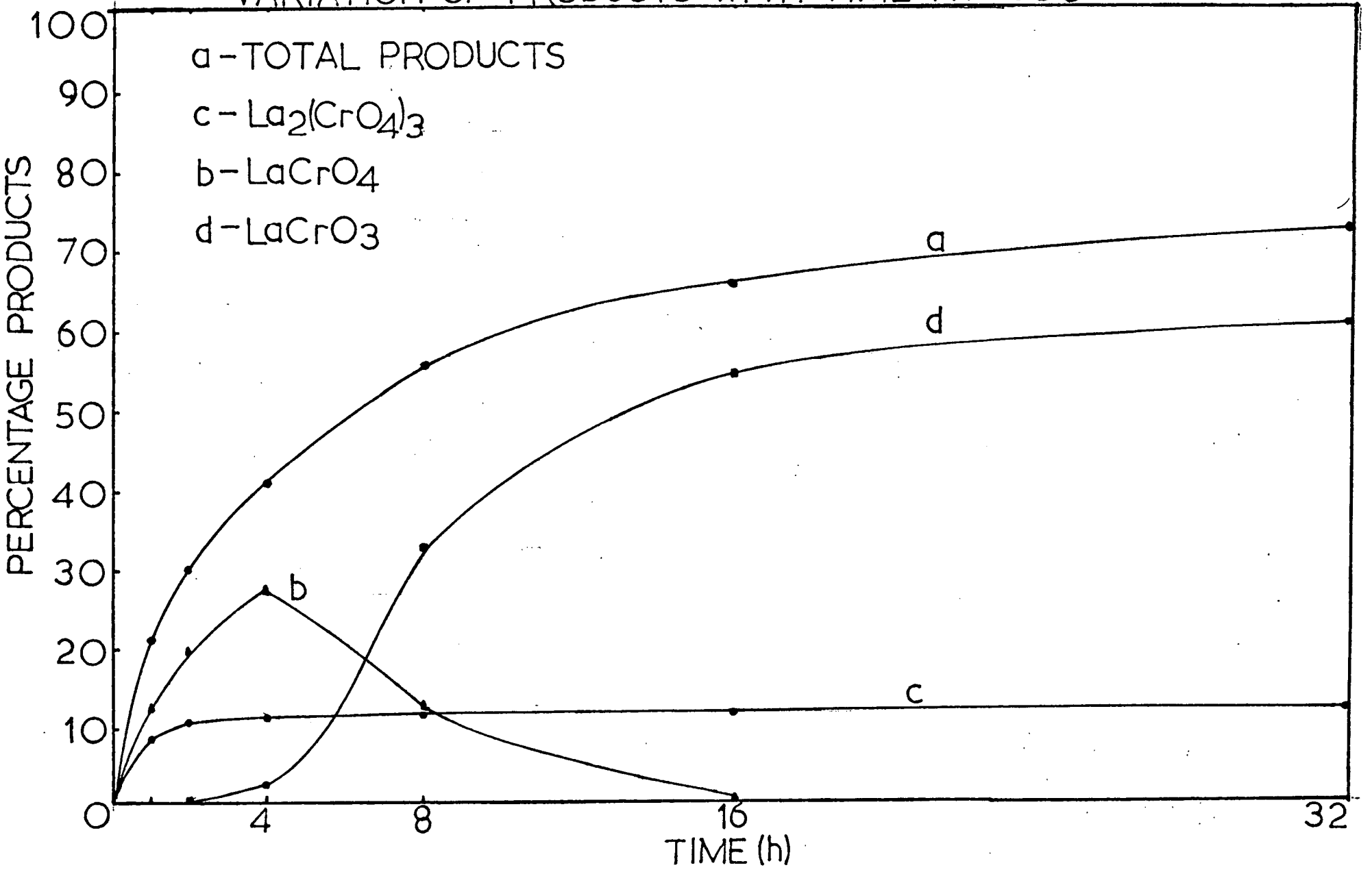


FIGURE 5

VARIATION OF PRODUCTS WITH TIME AT 620 °C

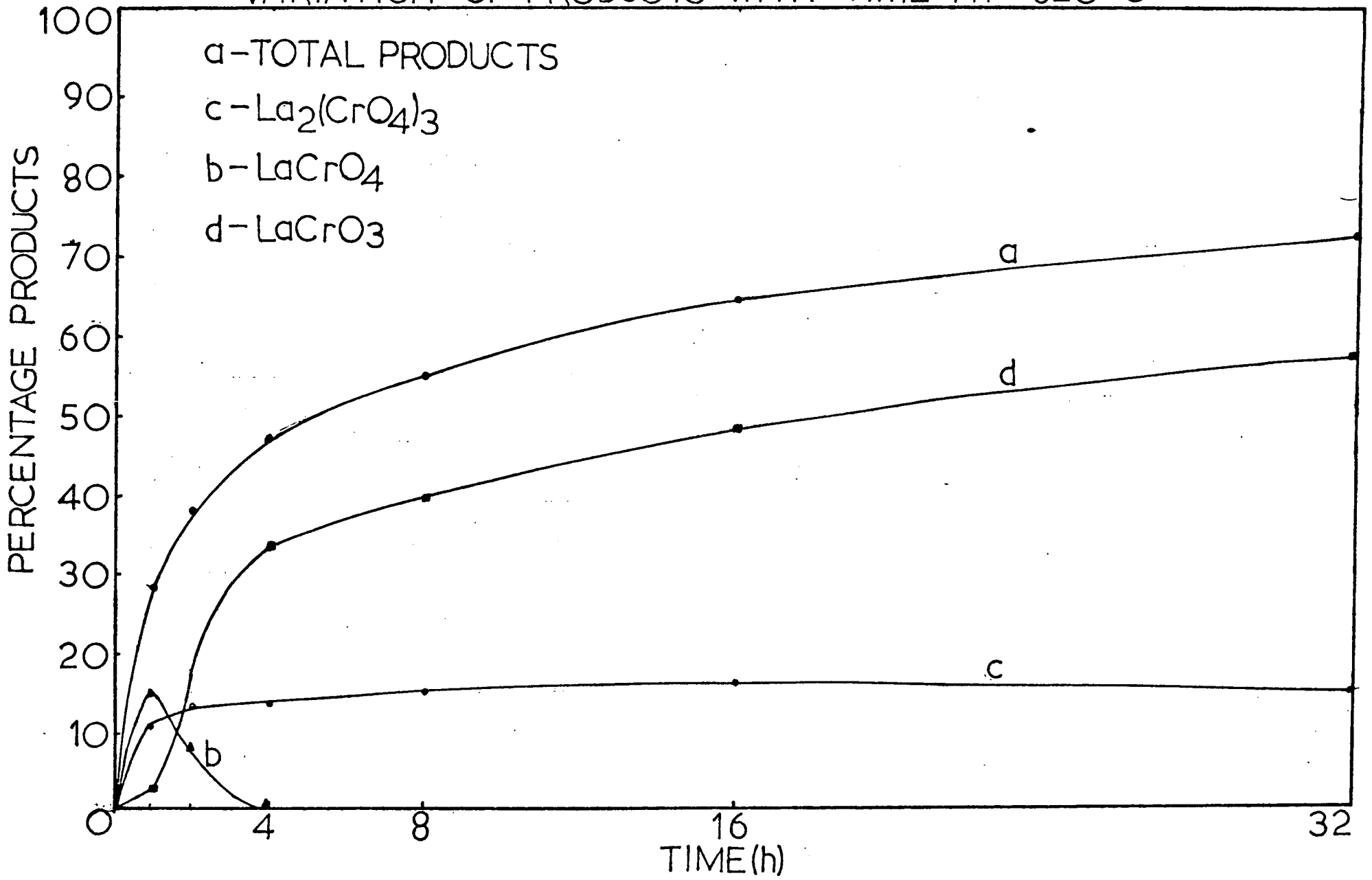


FIGURE 6

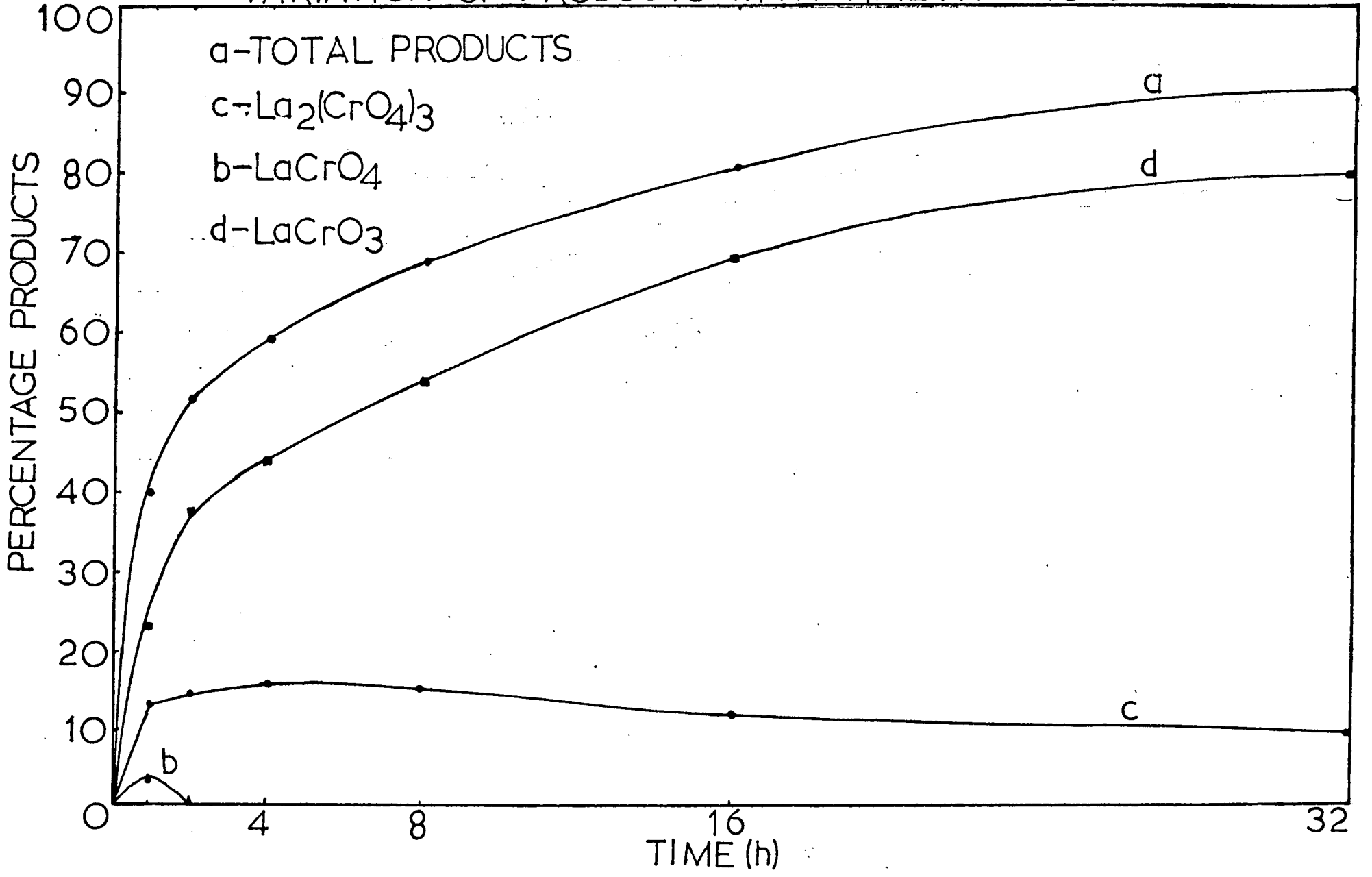

VARIATION OF PRODUCTS WITH TIME AT 640°C
a-TOTAL PRODUCTS
c-La2(CrO4)3
b-LaCrO4
d-LaCrO3
PERCENTAGE PRODUCTS
TIME (h)
0
10
20
30
40
50
60
70
80
90
100
4
8
16
32
a
d
c
b

FIGURE 7

ISOTHERMAL VARIATION OF $LaCrO_4$ (560 - 640°C)

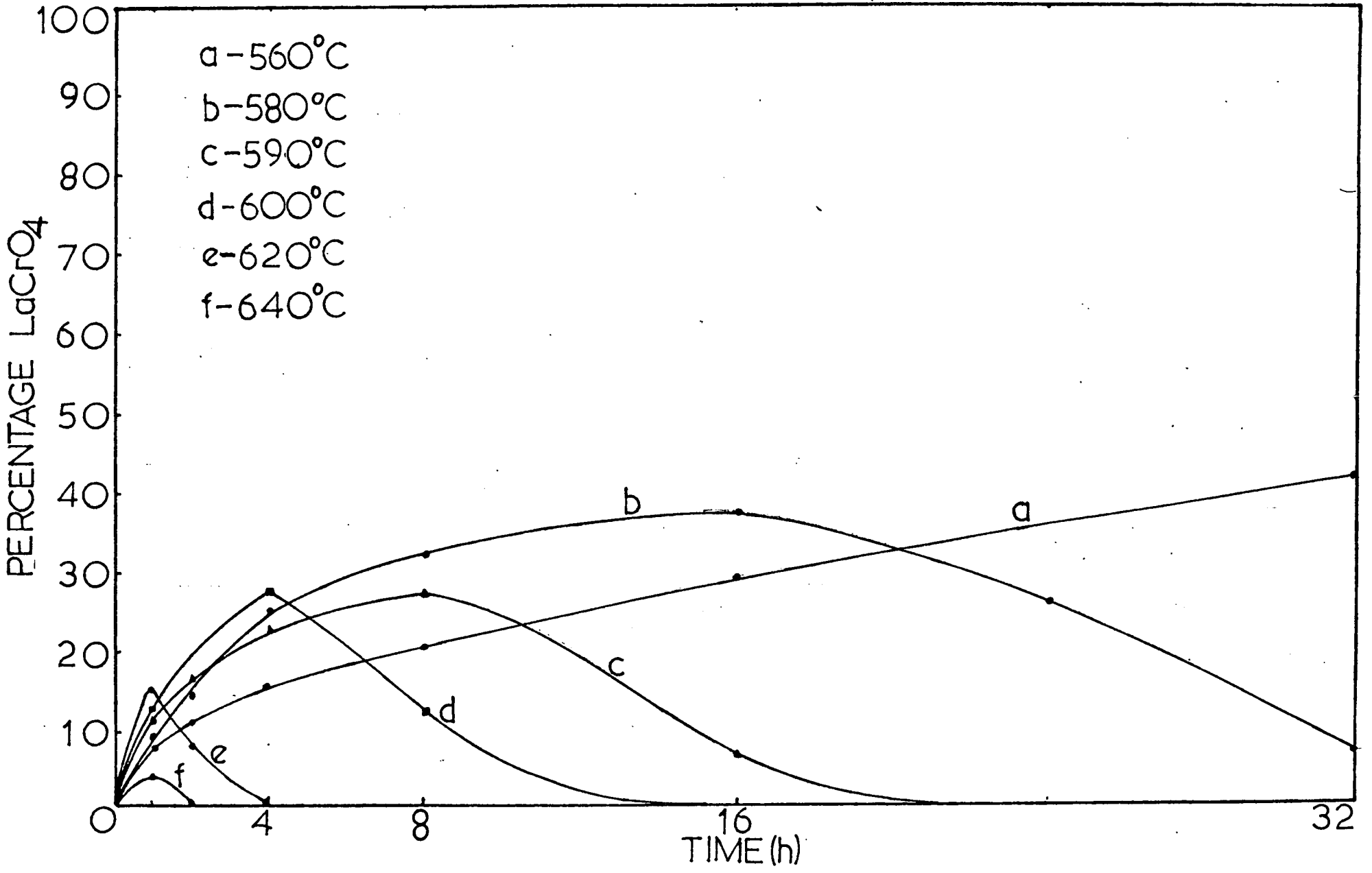


FIGURE 8

ISOTHERMAL VARIATION OF $LaCrO_3$ (580 – 640°C)

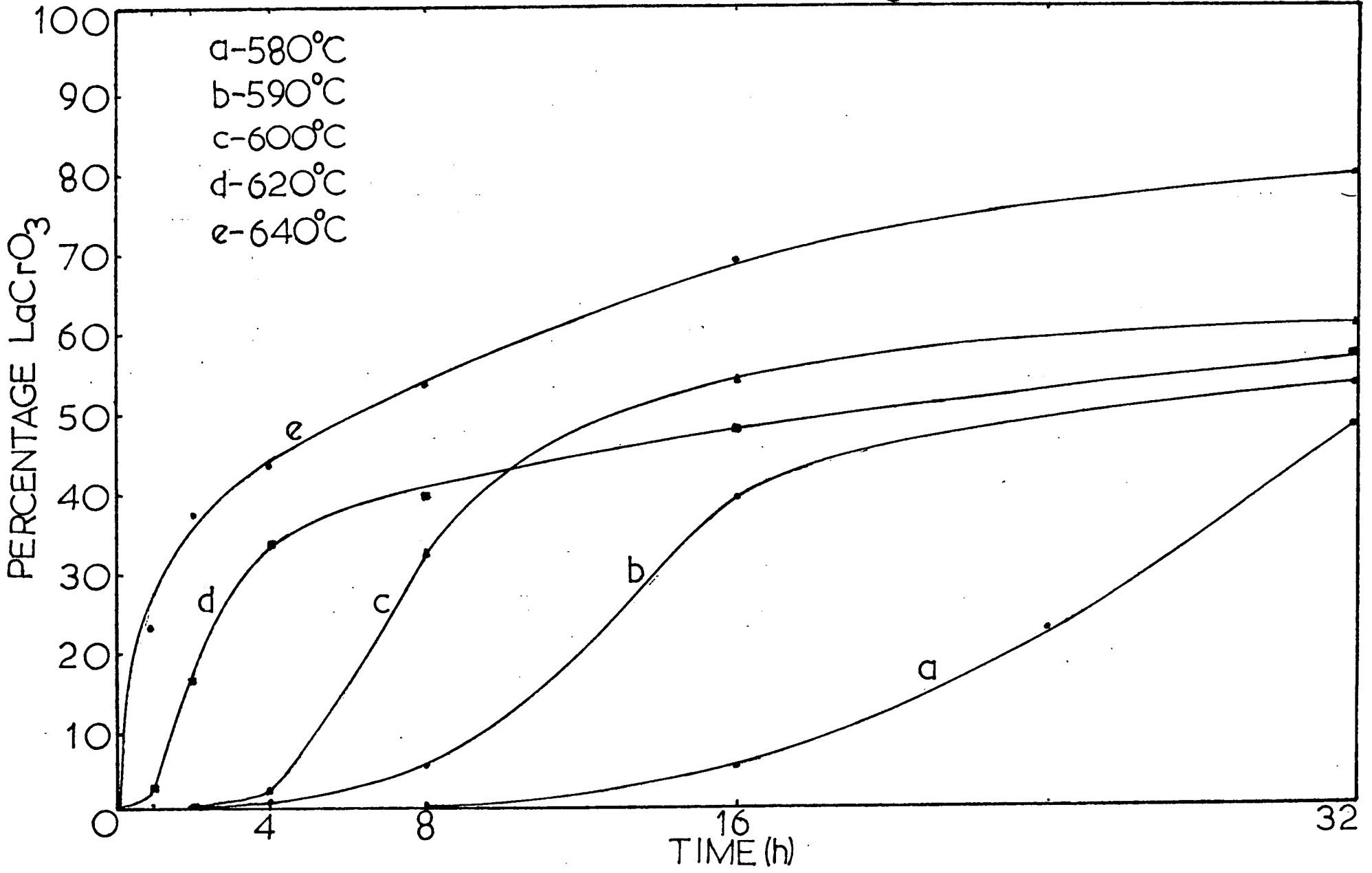


FIGURE 9

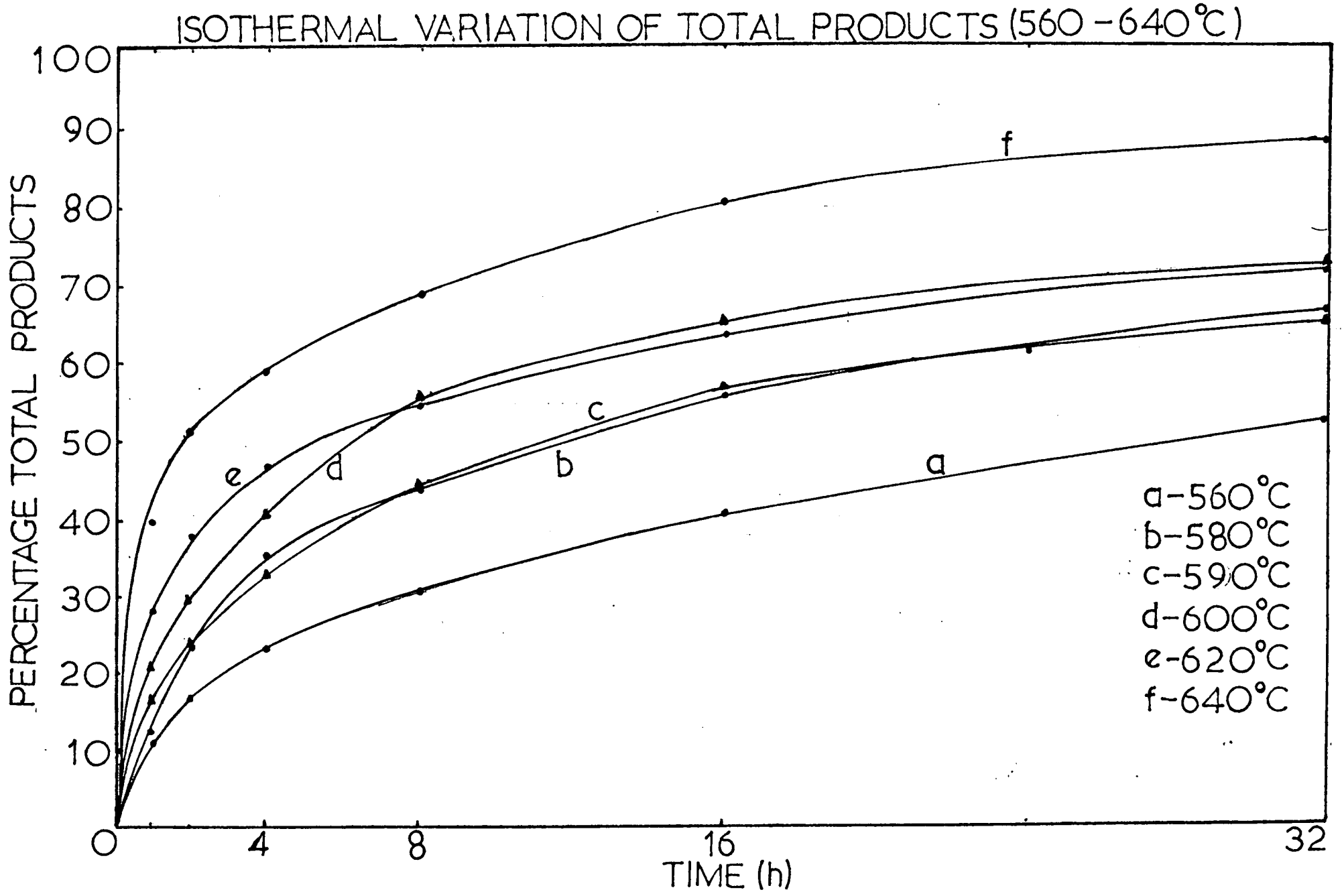

ISOTHERMAL VARIATION OF TOTAL PRODUCTS (560 - 640°C)
PERCENTAGE TOTAL PRODUCTS
100
90
80
70
60
50
40
30
20
10
0
4
8
16
32
TIME (h)
a
b
c
d
e
f
a-560°C
b-580°C
c-590°C
d-600°C
e-620°C
f-640°C

FIGURE 10

VARIATION OF [$LaCrO_4$ + $LaCrO_3$] WITH TIME AT 590°C

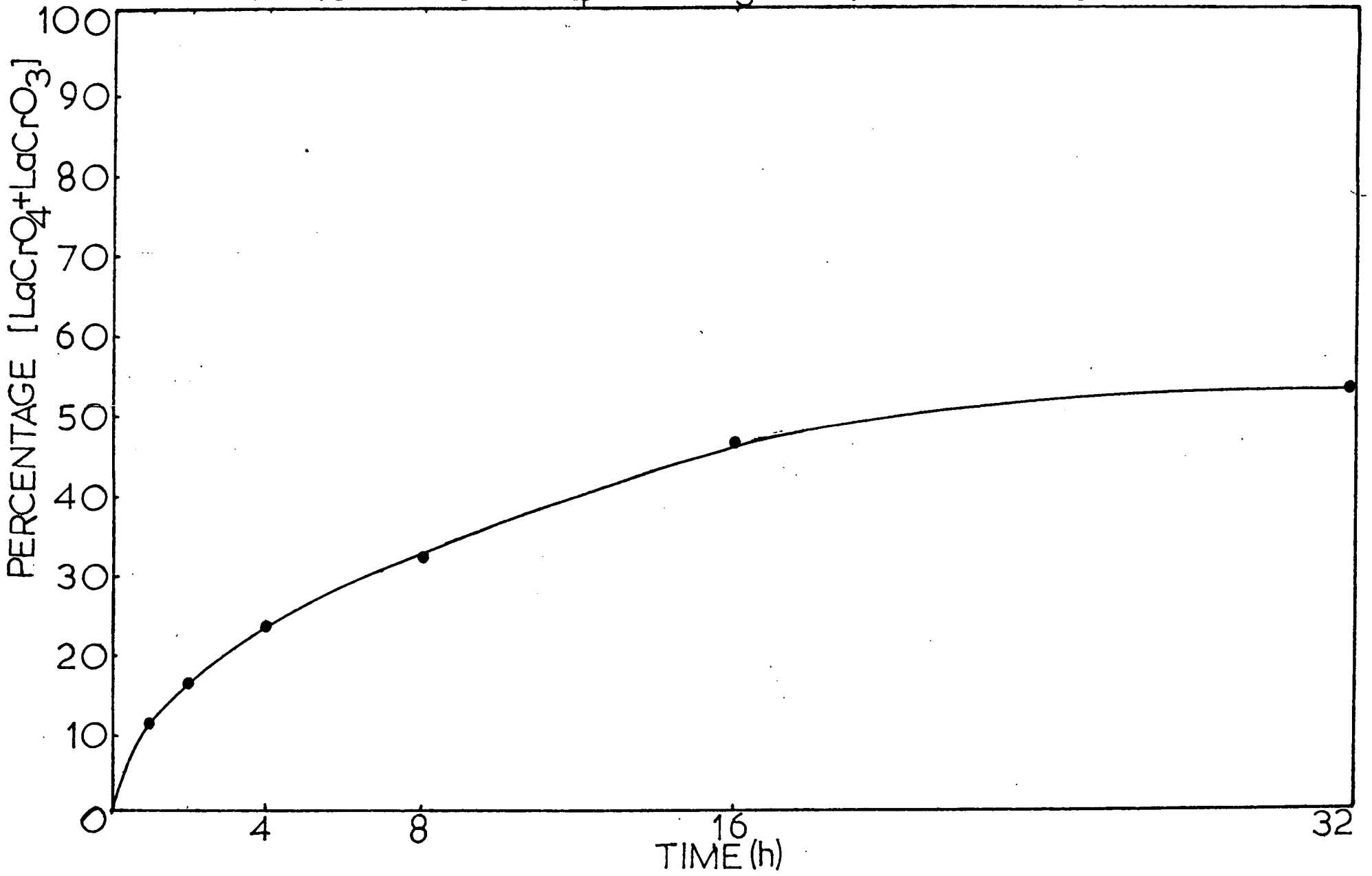


FIGURE 11

VARIATION OF [$LaCrO_3$ + $LaCrO_4$] WITH TEMPERATURE (600-680°C) IN OXYGEN.

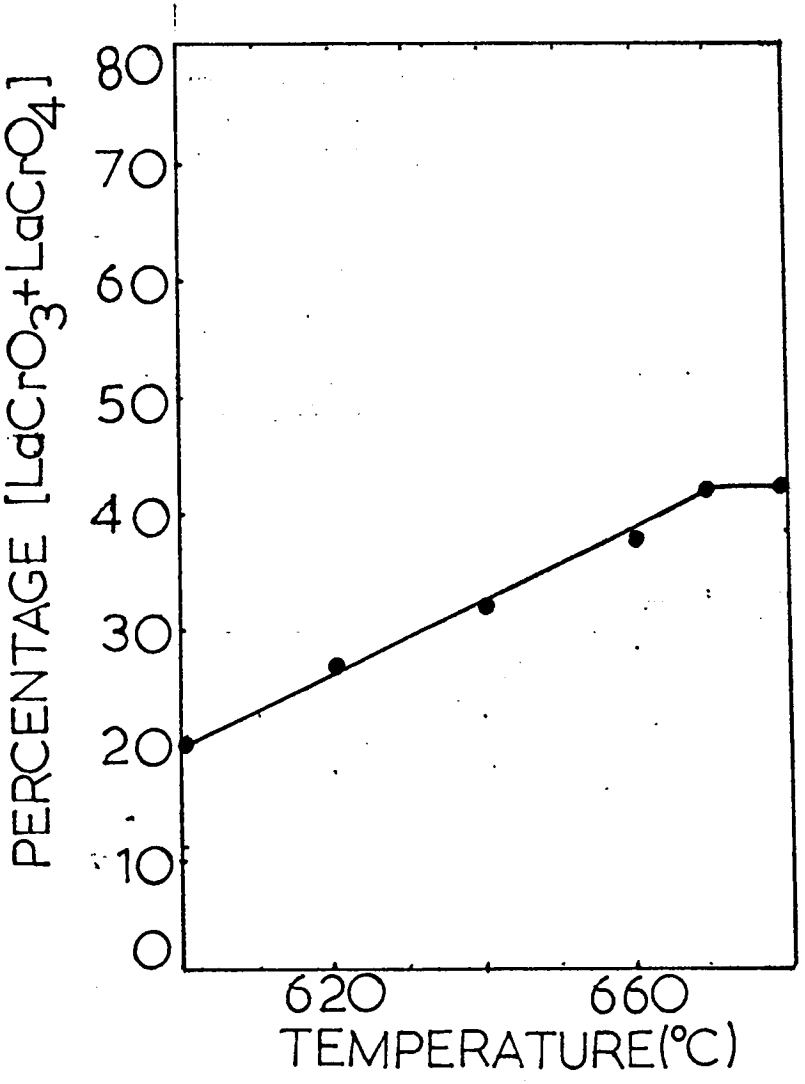


FIGURE 12

VARIATION OF [$LaCrO_3$ + $LaCrO_4$] WITH TEMPERATURE (500-620°C) IN AIR.

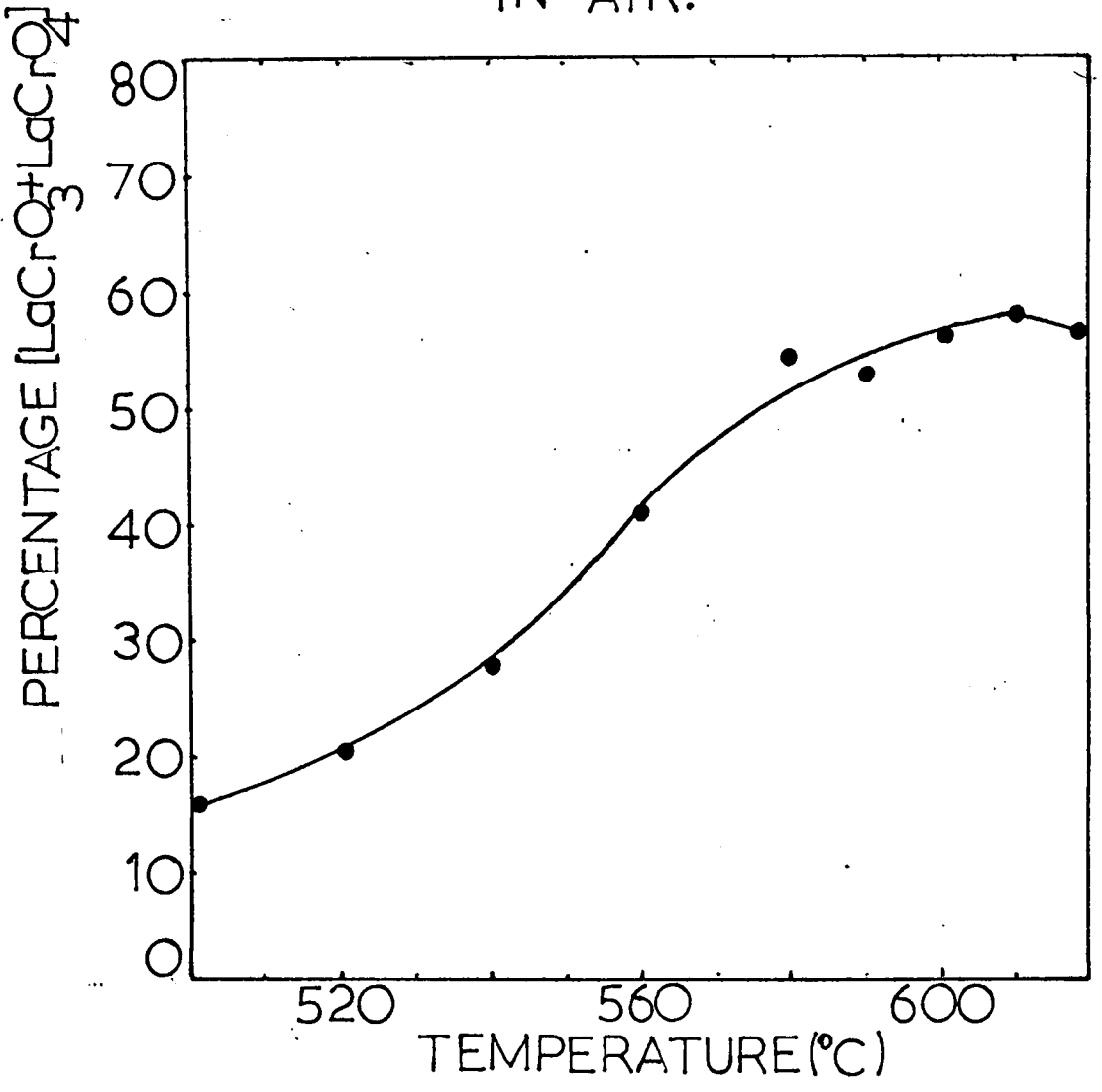


FIGURE 13

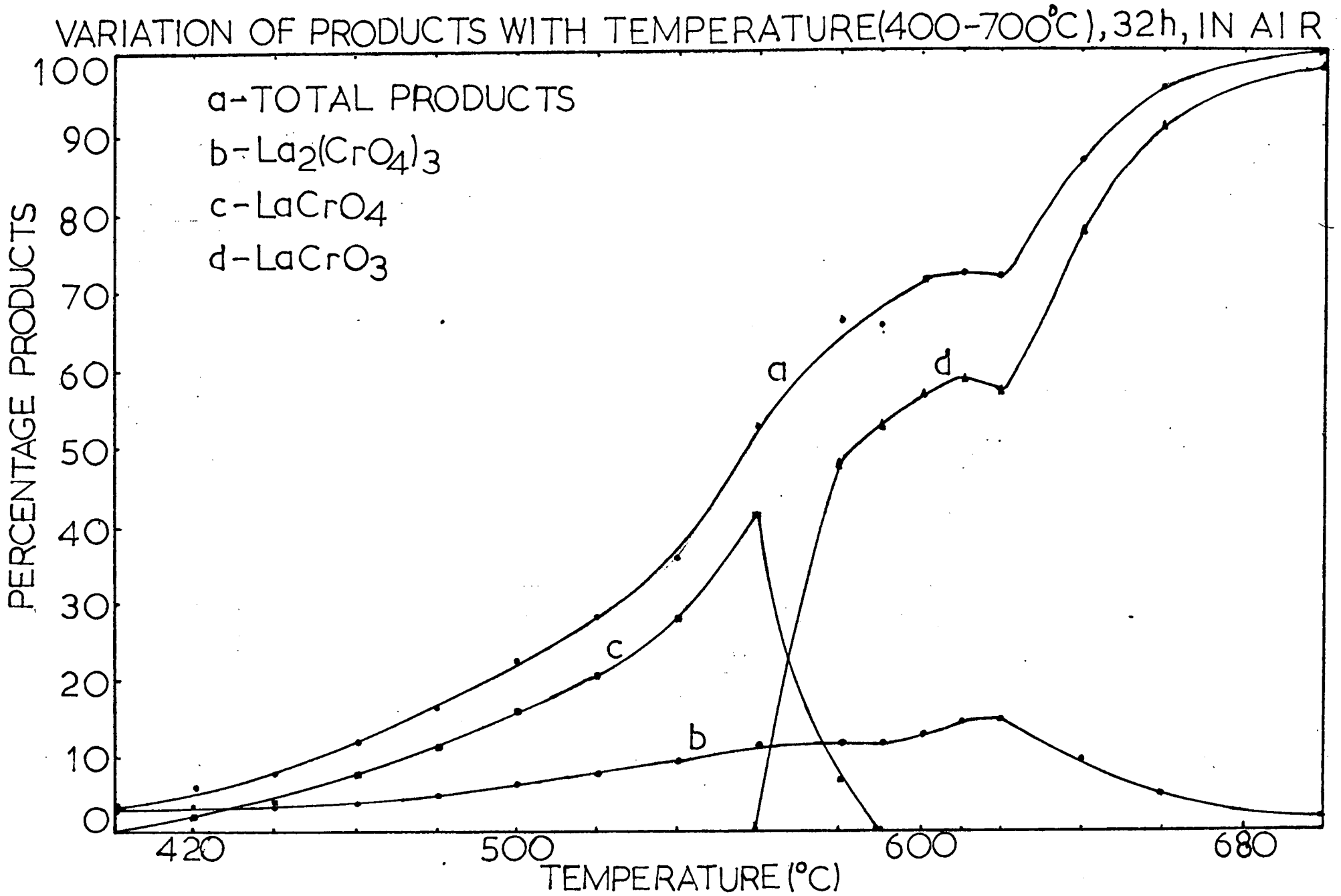

VARIATION OF PRODUCTS WITH TEMPERATURE(400-700°C), 32h, IN AIR
a-TOTAL PRODUCTS
b-La2(CrO4)3
c-LaCrO4
d-LaCrO3
PERCENTAGE PRODUCTS
100
90
80
70
60
50
40
30
20
10
0
420
500
600
680
TEMPERATURE (°C)
a
b
c
d

FIGURE 14

VARIATION OF PRODUCT WITH TEMPERATURE, 4h, IN ARGON

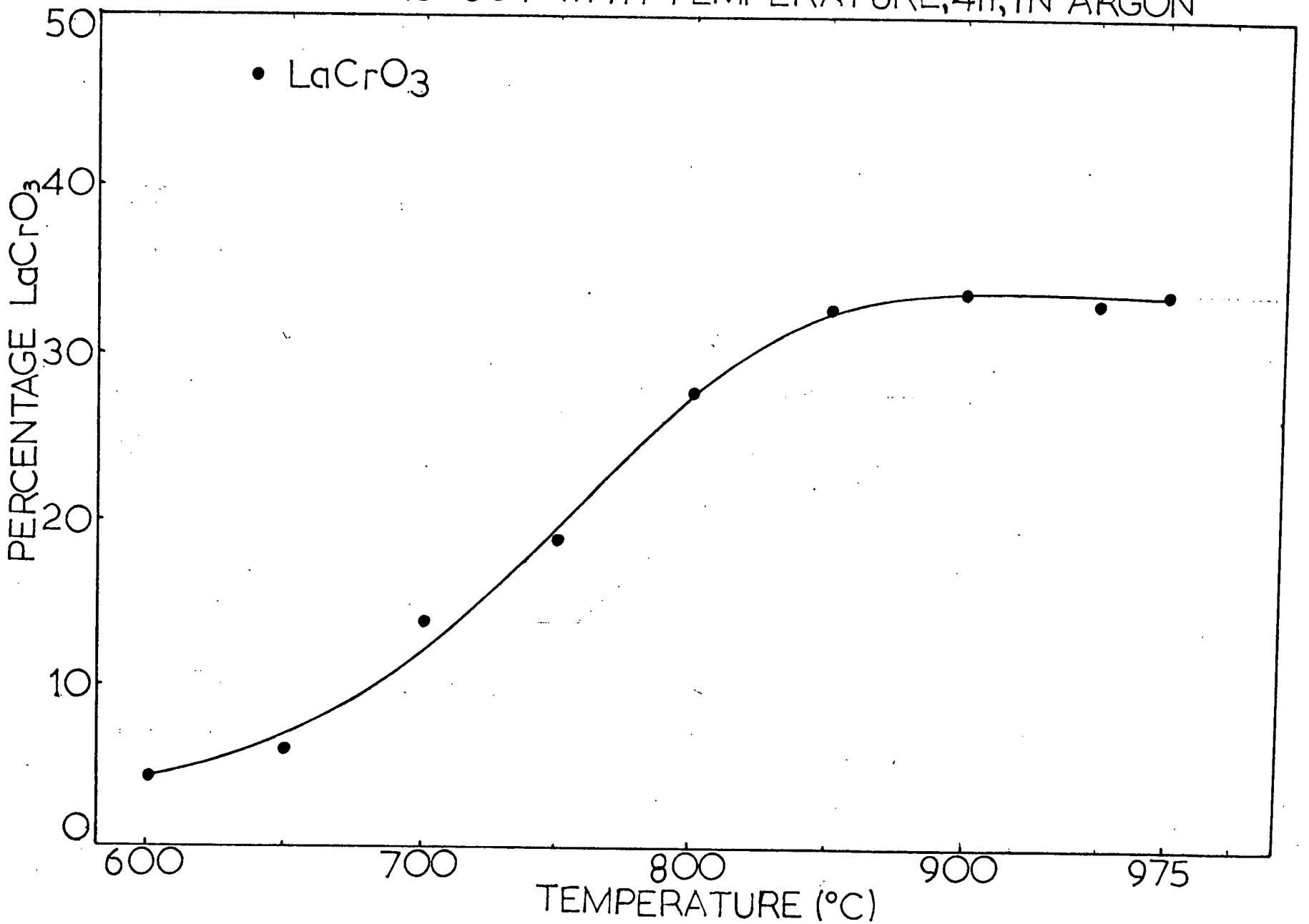


FIGURE 15

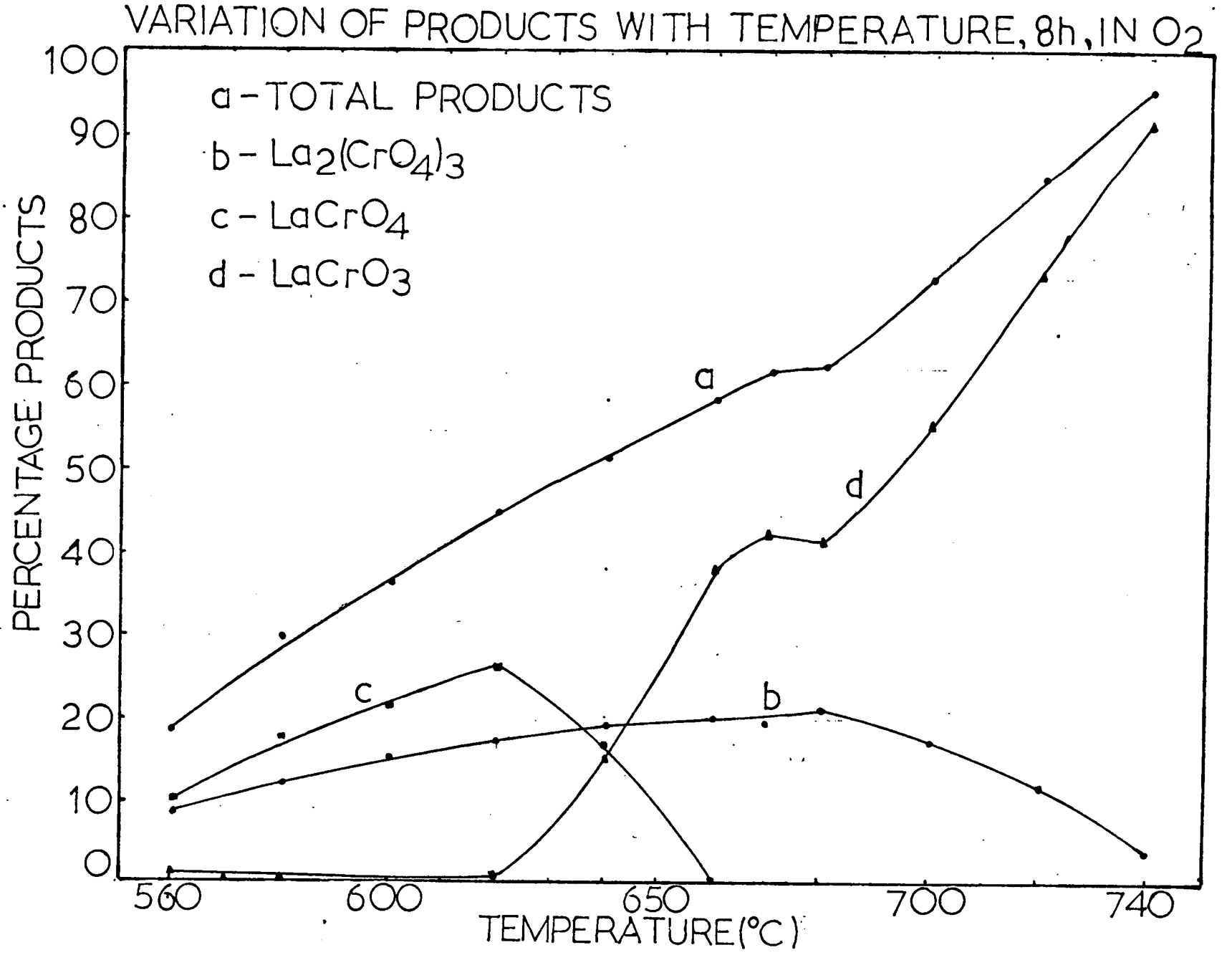
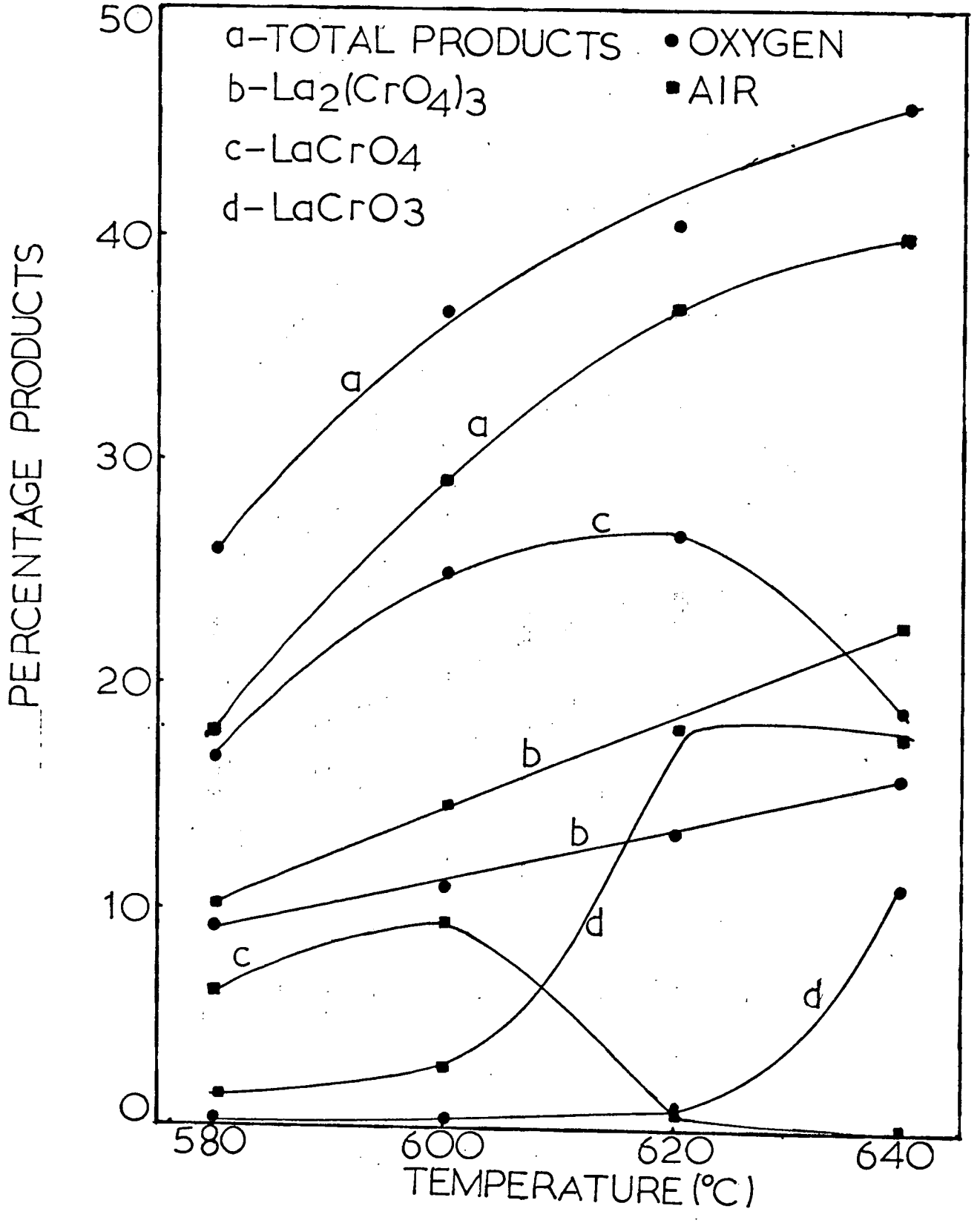

VARIATION OF PRODUCTS WITH TEMPERATURE, 8h, IN O_2
a - TOTAL PRODUCTS
b - $La_2(CrO_4)_3$
c - $LaCrO_4$
d - $LaCrO_3$
PERCENTAGE PRODUCTS
100
90
80
70
60
50
40
30
20
10
0
560
600
650
700
740
TEMPERATURE(°C)
a
b
c
d

FIGURE 16

COMPARISON OF PRODUCT VARIATION WITH TEMPERATURE (580–640°C), 4h, IN AIR AND OXYGEN



Physical data from reactions in the La_2O_3-Cr_2O_3 system

In the lanthanum oxide - chromic oxide system samples from selected reactions were investigated by the techniques of x-ray powder diffractometry and infra-red spectroscopy. The data obtained was tabulated, along with the experimental data for the products, prepared by standard methods, and the starting oxides.

(a) Infra-red Spectroscopy

Generally, the position and intensities of the absorptions in the infra-red are in very good agreement with those expected on the basis of the chemical analysis. The spectra for lanthanum chromate (V) prepared by the method of Schwarz (1963) agrees well with the spectra of $LaCrO_4$ obtained by Darrie(1967); and the two most prominent features of the spectra, absorptions at 812 cm^{-1} and 725 cm^{-1} appear in these samples in which chromate (V) was analysed, with intensities approximately in the order expected from the amounts determined by analysis.

Several bands in the infra-red of the reacted samples can be attributed to lanthanum chromate (VI) particularly those at approximately 935 cm^{-1}, 891 cm^{-1}, 858 cm^{-1} and 836 cm^{-1}. This grouping at these positions is characteristic of the chromates (VI) of the lanthanides. These bands from reacted samples differ, however, from the prepared anhydrous chromates (VI) in not having absorptions at 920 cm^{-1} and 904 cm^{-1}, which were also present in the spectra of the dehydrated lanthanum chromate (VI), obtained by Darrie (1967).

The bands in the spectra of the prepared anhydrous lanthanum chromate (VI), which were attributed by Darrie (1967) to anion-anion coupling, by analogy with the magnesium chromate (VI) compound, were those at 1000 cm^{-1} and 790-775 cm^{-1}.

It was obvious that a band at 1002 cm^{-1}, and a very strong band at 803 cm^{-1}, which were present in the spectra of the prepared sample of chromate (VI) were absent from the absorptions of the spectra for the reacted samples, which were shown by analysis to contain lanthanum chromate (VI). If the bands at 1002 cm^{-1} and 803 cm^{-1} are indeed due to anion-anion coupling then their absence would indicate the lack of such coupling in the structure of the chromate (VI) prepared during solid-state reaction.

The attribution of bands, in the spectra of reacted samples, to lanthanum chromite was more ambiguous, for the strongest bands in the chromite spectra overlap with bands of chromic oxide and chromate (V), but the intensities of absorptions indicate that the band 418-420 cm^{-1}, present in the absence of chromate (V), is due to lanthanum chromite.

(b) X-ray powder diffractometry

It was yet more difficult to assign lines in the x-ray powder diffraction pattern of reacted samples to products and starting oxides because of (i) overlap in positions of d-spacings, (ii) spurious surface effects, shown to be associated with the lanthanum oxide, i.e. depending on conditions of calcination, La_2O_3 can give a more

Infra-red absorption maxima of selected reactions in air for the La_2O_3-Cr_2O_3 system

590°C(8h)	540°C(32h)	580°C(24h)	560°C(32h)	600°C(16h)	640°C(8h)	620°C(8h)	700°C(32h)
930m	930w	932w	935w	938w	938w	935w	
885m	885m	890m	886m	893m	890m	891m	
855s, sp	856m, sp	858m, sp	858s, sp	856m	856m	858m	
	840m	840m	845s	840m	840m	836m	
810m	810m	810m	810m				
730m	725m	725m	729s				
638vs	639vs	638s	640s	630s	625s	630s	
580s	579s	585m	576m	590s	587s	585s	600vs
450w	448w	445w	445w			445w	
418m	418m	420m	420m	418s	418s	419s, sp	420s
380w	375w	384w	378w	385m, sp	383m	383m, sp	386m, sp
355w	355w	358w	355w	355w	355w	360w	360w
340w	340w	340w	343w	345w	342w	345w	339w, sp
				338w	334w		332w

Infra-red spectra of expected products, and reactants

$La_2(CrO_4)_3$	$LaCrO_4$	$LaCrO_3$	La_2O_3	Cr_2O_3
1002m, sp				
935vs				
920s, sp				
904s, sp				
860vs, sp	850m, sh			
826s, sp				
	812m			
803vs				
	725s			
				644s
		615vs		
				570s, sh
440w, sp			450m, sh	448m, sp
	421m	418s		418m, sp
385vw, sp	375w, sp	382m, sh		
	355w	355w		
348w, sp				
		330w	338s	

N.B. Numerals are in cm^{-1}, w = weak, m = medium, s = strong, v = very, sp = sharp, sh = shoulder.

d Å spacings for selected reactions for the La_2O_3-Cr_2O_3 system in air.

580°C(16h)	540°C(32h)	600°C(4h)	560°C(8h)	600°C(16h)	640°C(8h)	620°C(8h)
5.81(24)	5.70(36)	5.72(36)	5.63(42)	5.72(17)	5.74(11)	5.68(14)
				3.99(26)	3.89(20)	3.89(27)
3.68(24)	3.64(26)	3.64(23)	3.62(21)			
3.44(40)	3.40(43)	3.42(34)	3.40(27)			
3.30(43)	3.28(47)	3.27(43)	3.26(39)	3.21(21)	3.21(29)	3.21(35)
3.20(100)	3.20(100)	3.20(100)	3.19(100)	3.13(25)	3.13(25)	3.12(31)
3.15(33)		3.13(36)	3.12(24)			
3.10(33)	3.07(26)	3.08(41)	3.06(24)	3.07(18)	3.08(23)	3.07(31)
2.989(52)	2.995(52)	2.969(59)	2.960(33)			
2.780(29)				2.726(100)	2.763(100)	2.746(100)
	2.683(30)	2.675(32)	2.667(23)			2.667(20)
2.512(33)	2.488(26)	2.495(27)	2.478(26)			2.495(13)
2.301(24)	2.284(43)	2.287(45)	2.279(45)	2.298(13)	2.296(13)	2.287(19)
				2.257(23)	2.260(18)	2.246(23)
1.957(36)		1.941(23)		1.951(34)	1.953(32)	1.947(37)
		1.873(32)	1.870(29)			

The unbracketed numerals are d-spacings in Å, those not bracketed are intensity ratios.

d Å spacings of expected products and reactants.

$La_2(CrO_4)_3$	$LaCrO_4$	$LaCrO_3$	La_2O_3	Cr_2O_3
6.53(51)				
			5.63(92)	
5.44(43)				
4.58(36)				
		3.85(21)		
3.73(30)				
	3.58(23)			3.59(67)
3.48(21)			3.44(13)	
	3.37(63)			
			3.25(90)	
	3.16(100)		3.18(100)	
3.09(100)	3.05(17)			
2.931(26)	2.922(89)		2.931(19)	
2.899(51)				
2.841(15)			2.819(23)	
		2.730(100)		
	2.683(31)			2.644(97)
2.512(38)	2.522(21)			2.458(100)
			2.276(74)	
		2.230(19)		
	2.212(44)			
2.191(26)				2.161(43)
2.161(26)				
	1.996(46)			
		1.935(37)		
	1.928(29)			
			1.866(61)	

complicated pattern than that expected for the A-type La_2O_3 alone. This is particularly evident in reacted samples. (iii) The lack of agreement shown between the pattern of prepared anhydrous chromate (VI), sintered at 500°C for 1h. and lines in the powder pattern of reacted samples, shown to contain chromate (VI) from chemical analysis.

Nevertheless, lines due to $LaCrO_4$ and $LaCrO_3$ are clearly evident. For chromate (V), particularly the lines at d-spacings, between 3.62-3.68, 3.40-3.44 and 2.960-2.989 and those in the range 3.85-3.99 and 2.730-2.763 for lanthanum chromite.

(2) The Y_2O_3-Cr_2O_3 System

The variations of reaction products with temperature, in this system, were studied from 580-840°C in air, between 560-800°C in oxygen and from 620-800°C in an atmosphere of argon.

Variation of products with temperature in the range 580-840°C for times of 8 hours in air.

The results are given in Table 11, and are shown graphically in figure 17.

In the range 620-840°C yttrium chromite was formed, in addition, a chromate phase was found, although of such low yield that its nature could not be determined by analysis; but it was for the purpose of calculation, taken to be wholely yttrium chromate (VI). There was some justification for this, insomuchas the chromate does

TABLE 11 Results of temperature dependence in air

Temp(°C)	$Y_2(CrO_4)_3$	$YCrO_4$.	$YCrO_3$	Y_2O_3	Cr_2O_3	Total
580	0.84	-	-	58.48	39.81	99.13
620	0.57	-	3.12	52.48	38.69	99.86
660	0.37	-	12.73	51.78	34.90	99.78
700	0.20	-	17.64	48.68	32.82	99.34
740	0.13	-	21.87	46.45	31.29	99.74
780	0.13	-	24.37	45.01	30.26	99.77
840	0.13	-	26.30	43.76	29.50	99.69

not decompose completely before 600°C, as chromate (V) would be expected to do, on the evidence obtained from the lanthanum system. The results giving the yield for the chromate in Table 11 require further explanation, since the chromic oxide used contains soluble chromium,

$$\text{for sintered } Cr_2O_3, \quad \frac{\%\text{ soluble chromium}}{\text{unit weight of } Cr_2O_3} = 0.04\% \times 4$$

Therefore to be completely certain that the chromate analysed was product, only yields greater than 0.20% were regarded as significant.

Thus in air a chromate phase, less than 1%, was present between 580 and 700°C.

Yttrium chromite was first detected at 620°C, increasing with acceleration in the range from 620-approx. 630°C, as shown in figure 17. From 660°C where 12.73% formed, until 840°C with

26.30°/o, the yield of chromite increased steadily, with a marked decrease in the rate with temperature in the range 740-840°C.

Variation of product with temperature in the range 560-800°C in an oxygen flow, and between 620-800°C in an argon flow for times of 8 hours.

The yield of products obtained in these reactions are given in Table 12 for oxygen, and Table 13 for argon, and shown graphically in figure 18.

TABLE 12 Results of temperature dependence in oxygen

Temp.	$Y_2(CrO_4)_3$	$YCrO_4$	$YCrO_3$	Y_2O_3	Cr_2O_3	Total
560°C	1.31	-	-	58.97	39.45	99.73
580°C	1.38	-	-	58.84	39.46	99.68
620°C	0.81	-	5.44	55.67	37.65	99.57
660°C	0.17	-	15.04	50.31	34.03	99.55
700°C	0.24	-	19.10	47.59	32.32	99.25
740°C	0.20	-	22.12	46.07	31.10	99.49
800°C	0.13	-	27.18	43.36	29.14	99.81

TABLE 13 Results of temperature dependence in argon

Temp.	$Y_2(CrO_4)_3$	$YCrO_4$	$YCrO_3$	Y_2O_3	Cr_2O_3	Total
620°C	(0.13)	-	-	59.49	40.08	99.70
660°C	(0.13)	-	-	59.53	40.06	99.76
700°C	(0.17)	-	5.52	56.18	37.75	99.62
740°C	(0.17)	-	14.53	50.24	34.28	99.22
800°C	(0.16)	-	20.19	46.98	31.96	99.29

In oxygen between 560 and 620°C a chromate phase was present, although in higher yield than in air, the range in which it occured was not as extensive. In a similar way to that in air, in oxygen, the first decrease in the small amount of chromate present, from 1.38°/o at 580°C to 0.81°/o at 620°C coincided with the first appearance of yttrium chromite.

Yttrium chromite, then, was first detected at 620°C in oxygen, but with greater yield 5.44°/o as against 3.12°/o in air. An increase in the rate of formation with temperature was considered, from the graph, to occur from (600-630°C) approximately, with a slow decelerated formation from 660-800°C, although the deceleratory nature was not so marked above 740°C as in air. The difference in the initial increase in chromite formation at 620°C between air and oxygen atmospheres was maintained throughout the range in which they were comparable. The yield in oxygen was at all temperatures about 1-2°/o greater than in air.

In argon no chromate phase was detected, but chromite formed at temperatures of just below 700°C and above. The shape of the curve, figure 18, was similar to those obtained for reactions in air and oxygen, and it exhibited decay above 740°C.

Although the shape of the curves obtained in all three atmospheres would indicate the same mechanism, it is evident that the initial rates of reaction were enhanced in the order oxygen > air >> argon, and this occurs despite the small amounts of chromate formed in reactions in air and oxygen.

FIGURE 17

VARIATION OF PRODUCTS WITH TEMPERATURE, 8h, IN AIR

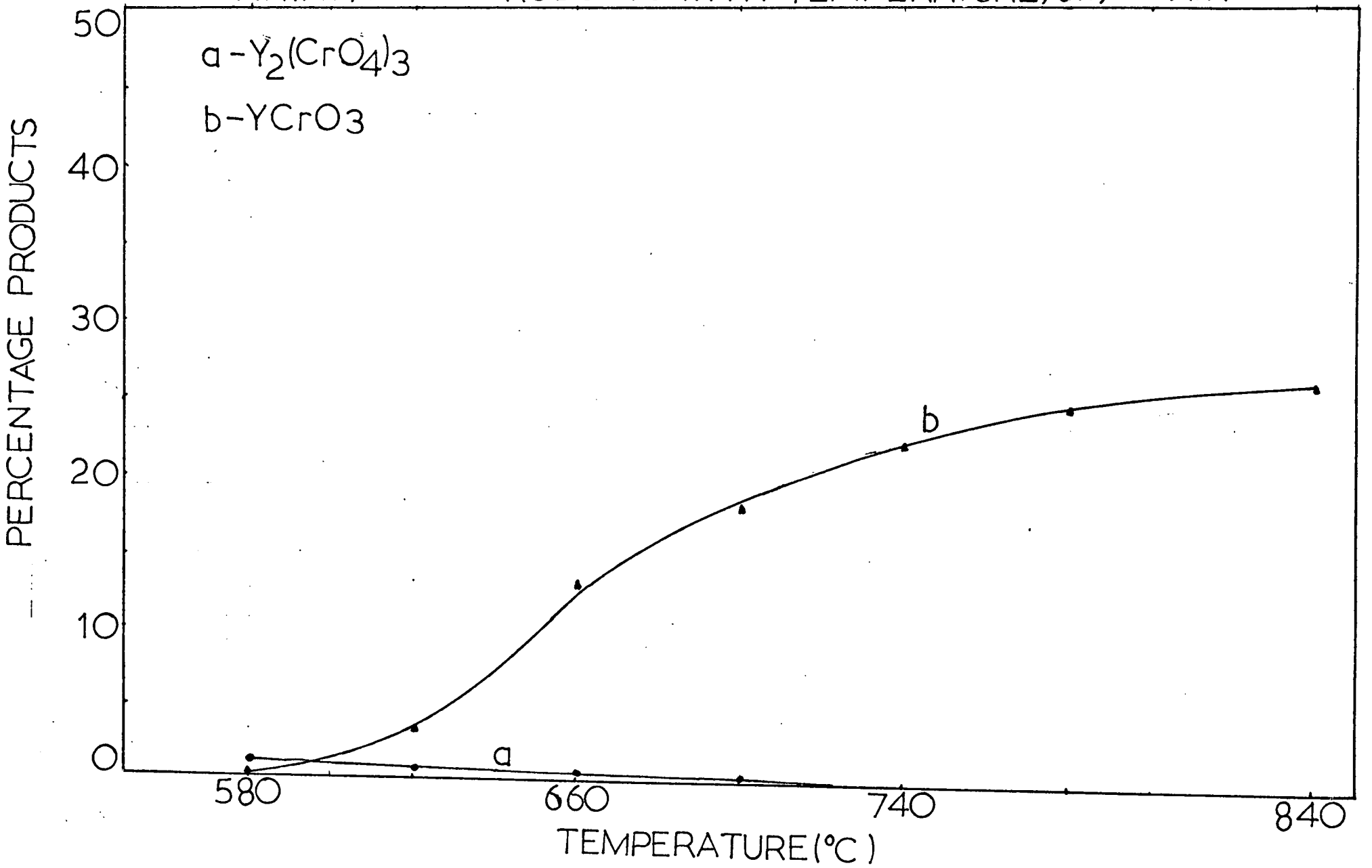
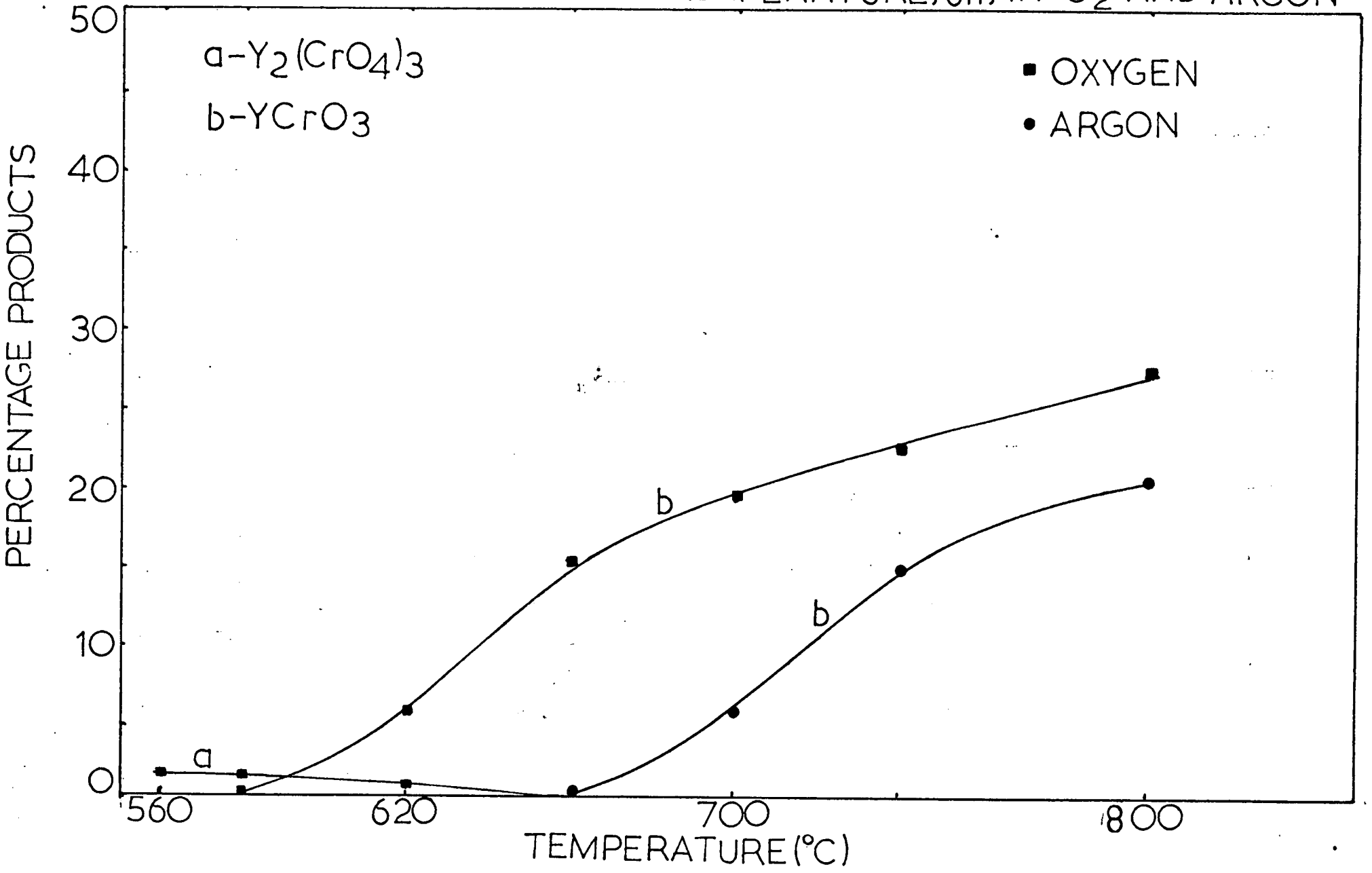


FIGURE 18

VARIATION OF PRODUCTS WITH TEMPERATURE, 8h, IN O_2 AND ARGON



(3) The Pr_2O_3-Cr_2O_3 system

The temperature dependence of reactions at a fixed time for this system was examined for periods of 8 hours within the temperature ranges 480-740° C in air, 500-720°C in oxygen and 600-840°C in argon.

Isothermal kinetics were also studied for temperatures between 560 and 680°C within the period 0-32 hours. Also, the extent of oxidation of the praseodymium (III) oxide was determined in air and oxygen atmospheres.

Temperature dependence in air in the range 480-740°C for times of 8 hours.

The results are given in Tables 14a and 14b and shown graphically in figures 19 and 20. Figure 19 shows the individual products and their sum, while figure 20, in addition to the yield of the individual products illustrates the variation of the unreacted praseodymium oxide separated into its two component oxidation states Pr(IV) and Pr(III). The variable oxidation state of the oxide was one of the main features of this system. Although the praseodymium oxide PrOx $1.5 < x < 2.00$ was of one phase, and each atom of praseodymium, from the evidence of $PrO_{1.833}(Pr_6O_{11})$, occupied identical sites in the praseodymium lattice (Eyring, 1962), the praseodymium atoms were not chemically indistinguishable. This was shown in one way by their ability to be separated through hydrolytic disproportionation during analysis, and in another way, by the

differing variations in the amounts of the Pr(IV) and Pr(III) components of the oxide, in the reactions studied here.

There formed two products praseodymium chromate (VI) and praseodymium chromite. The chromate was present at all temperatures in the range 480-740°C, while chromite was present only at temperatures of 600°C and above.

Praseodymium chromate (VI) formed steadily, with an increase in rate with temperature from 480-600°C. The rate of reaction slowed from 600°C to 620°C, where the maximum yield was obtained. From 620-640°C a relatively rapid decrease in product was observed, which was followed by a slower decrease continuing to 740°C.

Formation of the chromite commenced at 600°C, with a rate increasing with temperature until 640°C. Above 640°C the rate of formation showed a definite decrease with rise in temperature. The shape of the curve obtained for the chromite was simpler than that obtained in the lanthanum system, showing no intermediate maximum or minimum.

The plot of total product against temperature showed an increasing rate of formation up to 640°C and a decreasing rate above this temperature, with a small decrease in product from 680-700°C.

The Pr(IV) component of the unreacted oxide diminished with a decrease in rate with temperature between 480 and 620°C, and from 620 to 740°C little decrease was observed.

Praseodymium (III) increased in amount, slowly in the range 480-560°C, but more rapidly from 560°C, to a maximum at 600°C. From 600-660°C, praseodymium (III) diminished fairly rapidly with a decreasing rate, and subsequently only dropped a slight amount from 660-740°C.

In the range 480-600°C praseodymium (IV) alone decreased, while praseodymium chromate (VI) increased as did the praseodymium (III) component of the unreacted oxide. In this temperature range substantial amounts of chromite had not formed. Therefore to be consistent the decrease in the amount of Pr(IV) must be equal to the increase in Pr(III) of the oxide and the praseodymium content of the chromate (VI) formed, and so,

Praseodymium (IV) decreased by 12.5°/o, from graph

Praseodymium (III) increased by 5.0°/o, from graph.

Praseodymium chromate (VI) increased by 17.0°/o,

praseodymium content = 17.0 x 0.44.

= 7.5°/o.

Thus the results are consistent, within experimental error. There was no evidence to support the involvement of the Pr(III) component of the unreacted oxide in the formation of praseodymium chromate (VI). There was, however, a correlation between the Pr(III) component of the oxide and the formation of praseodymium chromite; whereas the decrease in chromate (VI) apparently does not coincide exactly with the increase in chromite.

Temperature dependence in oxygen in the range 500-720°C for times of 8 hours.

The results are displayed in Tables 15a and 15b and are shown plotted in figures 21 and 22. Figure 22 illustrates the variation of the unreacted praseodymium oxide and the products with temperature.

Only two products were present, praseodymium chromate (VI) and praseodymium chromite. Praseodymium chromate (VI) existed at all temperatures studied, while chromite only formed in significant amounts above 620°C, although present in amounts of less than 1% at 580 and 600°C.

Chromate increased from 500-600°C, with an increase in rate of formation with temperature, but slowly from 600°C to a maximum at 620°C. The first significant decrease of product occurred in the 640-660°C temperature range. This was the largest rate of decrease,and from 660-720°C the decrease continued at a slower rate.

Praseodymium chromite formed rapidly with an increasing rate of formation from 620 to 660°C and a slightly decreasing rate above 660°C.

Praseodymium (IV) diminished with a decrease in rate with temperature from 480-600°C. . Between 600 and 720°C the rate of decrease was considerably slower.

The praseodymium (III) component of the unreacted

praseodymium oxide increased in the range 500-620°C, and decreased thereafter, with the largest drop occurring between 640 and 660°C.

TABLE 14a Temperature dependence in air (8h).

Temp(°C)	$Pr_2(CrO_4)_3$	$PrCrO_4$	$PrCrO_3$	x	PrO_x	Cr_2O_3	Total
480	4.44	-	-	1.778	66.15	29.68	100.27
520	6.26	-	-	1.771	64.86	28.92	100.04
540	7.43	-	-	1.766	63.95	28.31	99.69
560	11.31	-	-	1.753	61.95	27.35	100.61
580	14.62	-	-	1.725	59.83	25.86	100.31
600	21.41	-	-	1.694	56.59	22.85	100.85
620	23.10	-	15.78	1.676	44.49	17.55	100.92
640	16.16	-	35.85	1.706	34.77	14.02	100.80
660	14.18	-	42.04	1.737	31.70	12.38	100.30
680	12.16	-	46.02	1.751	30.41	11.90	100.49
700	8.52	-	48.25	1.759	31.06	12.90	100.73
740	7.03	-	49.75	1.766	30.93	13.01	100.70

TABLE 14b Variation in oxidation state of the unreacted oxide, 8h in air.

Temp (^{o}C)	480	520	540	560	580	600	620	640	660	680
Pr^{4+} (^{o}/o)	30.56	29.26	28.34	26.20	22.55	18.42	13.12	12.00	12.53	12.72
Pr^{3+} (^{o}/o)	25.39	24.75	24.91	25.48	27.46	29.06	24.24	17.12	13.95	12.65

Temp (^{o}C)	700	740
Pr^{4+} (^{o}/o)	13.46	13.70
Pr^{3+} (^{o}/o)	12.43	12.06

TABLE 15a Temperature dependence in oxygen (8h).

Temp(^{o}C)	$Pr_2(CrO_4)_3$	$PrCrO_4$	$PrCrO_3$	x	PrO_x	Cr_2O_3	Total
500	5.65	-	-	1.796	65.56	29.17	100.38
540	9.57	-	-	1.771	63.63	27.68	100.28
580	18.21	-	0.77	1.724	57.60	25.18	101.76
600	27.31	-	0.84	1.646	50.95	20.59	99.25
620	30.94	-	3.54	1.617	47.54	18.66	100.68
640	30.78	-	12.67	1.614	42.04	15.72	101.21
660	16.48	-	51.96	1.638	23.07	8.28	99.79
680	11.63	-	65.91	1.646	16.31	6.57	100.42
720	4.04	-	89.08	1.559	5.06	1.59	99.77

TABLE 15b Variation in oxidation state of the unreacted oxide, 8h in oxygen.

Temp. (°C)	500	540	580	600	620	640	660	680	720
Pr^{4+}	32.21	28.45	21.56	12.55	9.37	8.07	5.35	4.00	0.51
Pr^{3+}	22.25	24.03	26.61	30.38	30.80	27.46	14.10	9.74	3.79

As stated the Pr(III) component of the unreacted oxide did not decrease until 620°C, at which temperature 3.54% chromite had formed. This decrease of Pr(III) occurred 20°C before a decrease in chromate (VI) was observed, but the largest decrease in both Pr(III) and $Pr_2(CrO_4)_3$ took place in the same temperature range, 640-660°C.

The decrease in the amount of praseodymium (IV) between 500 and 600°C could be accounted for by the increase in praseodymium (III) unreacted oxide and the praseodymium in the chromate (VI). It could also be seen that the formation of the chromite was a complex process involving at least two distinct sources of praseodymium, i.e. from the chromate (VI) and praseodymium (III) of the oxide.

Comparison of the results of the temperature dependence in air and oxygen.

The noteable changes are not those of the nature and type of processes, which appear to take place, but of extent.

At all temperatures over which comparison can be made

the yield of chromate (VI) in oxygen was greater than that in air. In air, as in oxygen, decrease of the Pr(III) component of the unreacted oxide began at a temperature 20°C below the apparent commencement of decrease of $Pr_2(CrO_4)_3$, but in air these respective decreases occurred 20°C lower than the corresponding decreases in oxygen. That this is so indicates some relationship between the decrease in Pr(III) of the oxide and praseodymium chromate (VI). The formation of praseodymium chromite in amounts greater than 2% also begins 20°C higher in oxygen than in air, and has an initial rate of formation which is faster in air than oxygen. However, from approximately 650-720°C chromite formed in air was less than that formed in oxygen.

In most other ways, the extents of formation, extents of depletion, initial and subsequent rates of formation, initial and subsequent rates of depletion, were greater in oxygen than air.

The oxidation of praseodymium (III) oxide in air and oxygen atmospheres.

This was studied at times of 8 hours alternatively in air and oxygen atmospheres at temperatures of 560°C, 600°C and 660°C.

The extent of oxidation of the praseodymium (III) oxide is shown in the table below as the mean oxidation state x.

Temperature	Atmosphere	Value of x
560°C	Air	1.834
	O_2	1.836
600°C	Air	1.834
	O_2	1.835
660°C	Air	1.836
	O_2	1.837

Therefore within experimental error both in air and oxygen the formula of the praseodymium oxide could be given as Pr_6O_{11}, i.e. x = 1.833.

Note that in the reactions carried out isochronously that the oxide never attains this extent of oxidation. For the purposes of comparison the mixture $Pr_6O_{11} : Cr_2O_3$ would contain 37.78°/o Pr(IV) and 19.46°/o Pr(III).

Reaction of the praseodymium (III) oxide for 1 min . at 600°C in air produced a praseodymium oxide with a degree of oxidation given by x = 1.779.

Temperature dependence in argon in the range 600-840°C for times of 8 hours.

The results are given in Table 16, and shown graphically in figure 23.

TABLE 16 Results of temperature dependence in argon (8h).

Temp(^{o}C)	$Pr_2(CrO_4)_3$	$PrCrO_4$	$PrCrO_3$	Pr_2O_3	Cr_2O_3	Total
600	-	-	5.01	65.04	30.00	100.05
640	-	-	10.19	61.49	28.37	100.05
680	-	-	18.12	56.10	23.78	100.00
720	-	-	27.41	49.74	22.90	100.05
750	-	-	36.33	43.43	20.01	99.77
780	-	-	46.13	36.71	17.14	99.98
840	-	-	59.43	27.65	12.80	99.88

The only product was praseodymium chromite, and the unreacted praseodymium oxide had only one oxidation state Pr(III).

At 600^{o}C, 5.01^{o}/o praseodymium chromite had formed, this was higher at this temperature than that present in either air or oxygen. The rate of formation of chromite increased with temperature from 600 to 780^{o}C, but decreased above 780^{o}C. The amount of chromite formed, although less than that in air and oxygen was yet very large, almost 60^{o}/o chromite was present at 840^{o}C.

The graph was simpler than those obtained for plots in air and oxygen, with the general characteristics of the temperature dependence curves for the system La_2O_3-Cr_2O_3 in argon, and the system Y_2O_3-Cr_2O_3 in oxygen, air and argon. Again only one mechanism was indicated by the results or seems likely to occur in an argon atmosphere.

Isothermals at 560°C, 600°C, 620°C, 630°C, 640°C and 680°C.

The results at each temperature expressed as weight per cent product are given in Tables 17a to 22a, and the plots per cent by weight product against time are shown in figures 24-29, along with the total product. The praseodymium in oxidation states (III) and (IV), components of the unreacted oxide, are given separately in Tables 17b to 22b, and their variation with time shown in figures 30-35, with the yields of the individual products.

Three products were present in these isothermals; praseodymium chromate (VI) at all temperatures and for all times; praseodymium chromite, in amounts greater than 1°/o, only at temperatures of 600°C and above; while, praseodymium chromate (V) was found only at 560°C. In addition, the unreacted praseodymium oxide again exhibited a variable oxidation state.

The rate of formation of praseodymium chromate (VI), at all temperatures, decreased with time, from zero reaction time. This was more pronounced as the temperature was raised because the initial rate of formation increased with rise in temperature.

The maxima of chromate (VI) formation appeared after successively shorter reaction periods as the temperature was raised. Thus at 600°C the maxima occurred at 16 hours, at 620°C after 8 hours, at 630°C after 4 hours, at 640°C after 2 hours, and with a maximum at 680°C after 1 hour. There was also a reduction in the amount of chromate (VI) constituting the maximum with rise in temperature from 25.32°/o at 600°C to 15.71°/o at 680°C.

TABLE 17a Results of 680°C isothermal

Time (h)	$Pr_2(CrO_4)_3$	$PrCrO_4$	$PrCrO_3$	x	PrO_x	Cr_2O_3	Total
1	15.71	-	17.17	1.669	47.41	19.93	100.22
2	15.35	-	25.65	1.689	42.18	17.53	100.71
4	13.32	-	32.67	1.704	37.99	16.27	100.25
8	12.20	-	39.44	1.762	33.91	14.04	99.59
16	12.64	-	46.32	1.745	29.37	11.92	100.25
32	10.99	-	51.60	1.740	26.42	10.42	99.43

TABLE 17b Variation in oxidation state of the unreacted oxide at 680°C

Time(h)	1	2	4	8	16	32
Pr(IV)	13.50	13.38	13.03	14.82	12.00	10.57
Pr(III)	26.36	22.01	22.57	13.44	12.51	11.49

TABLE 18a Results of 640°C isothermal

Time (h)	$Pr_2(CrO_4)_3$	$PrCrO_4$	$PrCrO_3$	x	PrO_x	Cr_2O_3	Total
1	16.03	-	4.24	1.692	56.24	24.18	100.69
2	19.87	-	7.54	1.705	51.03	21.43	99.87
4	16.92	-	21.63	1.728	44.41	17.78	100.74
8	16.24	-	35.33	1.701	35.34	13.90	101.01
16	12.24	-	47.07	1.777	29.80	11.74	100.85
32	10.56	-	53.43	1.777	24.97	8.81	99.67

TABLE 18b Variation in oxidation state of the unreacted oxide, at 640°C.

Time(h)	1	2	4	8	16	32
Pr(IV)	18.13	17.56	16.90	11.90	13.75	11.52
Pr(III)	29.04	23.19	20.23	17.72	11.05	9.26

TABLE 19a Results of 630°C isothermal

Time (h)	$Pr_2(CrO_4)_3$	$PrCrO_4$	$PrCrO_3$	x	PrO_x	Cr_2O_3	Total
1	14.30	-	3.44	1.715	58.54	25.08	101.36
2	18.09	-	5.91	1.685	53.88	23.16	101.04
4	21.08	-	11.01	1.679	48.84	20.15	101.08
8	16.80	-	29.82	1.683	38.20	13.68	100.50

TABLE 19b Variation in oxidation state of the unreacted oxide at 630°C

Time(h)	1	2	4	8
Pr(IV)	21.07	16.74	14.69	11.72
Pr(III)	27.93	28.49	24.33	21.87

TABLE 20a Results of 620°C isothermal

Time (h)	$Pr_2(CrO_4)_3$	$PrCrO_4$	$PrCrO_3$	x	PrO_x	Cr_2O_3	Total
1	11.63	-	0.91	1.735	61.26	26.58	100.38
2	16.84	-	0.67	1.708	56.38	24.96	100.85
4	21.00	-	4.79	1.678	53.89	21.39	101.03
8	22.09	-	15.08	1.686	45.51	18.20	100.88
16	17.25	-	33.48	1.716	35.53	14.16	100.42
32	12.56	-	51.90	1.740	25.11	9.92	99.49

TABLE 20b Variation in oxidation state of the unreacted oxide at 620°C.

Time(h)	1	2	4	8	16	32
Pr(IV)	24.10	20.37	16.13	14.27	12.85	10.08
Pr(III)	27.08	28.53	29.14	23.93	16.89	10.91

TABLE 21a Results of 600°C isothermal

Time (h)	$Pr_2(CrO_4)_3$	$PrCrO_4$	$PrCrO_3$	x	PrO_x	Cr_2O_3	Total
1/4	4.32	-	-	1.773	66.25	29.67	100.24
1	8.84	-	-	1.754	63.24	28.24	100.48
2	10.82	-	0.67	1.738	62.33	26.64	100.46
4	16.20	-	0.80	1.707	58.80	23.54	100.34
8	22.29	-	2.48	1.669	53.75	21.67	100.19
16	25.32	-	10.57	1.628	46.32	17.76	99.97
32	16.72	-	37.90	1.706	32.56	12.69	99.87

TABLE 21b Variation in oxidation state of the unreacted oxide at 600°C.

Time(h)	1/4	1	2	4	8	16	32
Pr(IV)	30.10	26.76	24.83	20.42	15.25	11.33	11.22
Pr(III)	25.05	23.48	27.23	28.83	29.92	27.76	16.06

TABLE 22a Results of 560°C isothermal

Time (h)	$Pr_2(CrO_4)_3$	$PrCrO_4$	$PrCrO_3$	x	PrO_x	Cr_2O_3	Total
1	2.18	4.59	-	1.786	64.13	29.51	100.41
2	2.98	5.93	-	1.766	62.92	28.83	100.66
4	2.58	8.60	-	1.776	61.61	27.90	100.69
8	6.46	6.52	1.28	1.761	59.78	26.34	100.38
16	10.60	6.37	-	1.738	57.66	25.64	100.33
32	17.04	2.96	1.42	1.666	55.66	23.38	100.46

TABLE 22b Variation in oxidation state of the unreacted oxide at 560°C.

Time(h)	1	2	4	8	16	32
Pr(IV)	30.47	27.89	28.28	25.95	22.94	18.65
Pr(III)	22.85	24.52	22.99	23.82	25.21	28.16

The rate of decrease of chromate (VI) diminished with time. This was again accentuated, at longer times, as the temperature increased because the initial rate of decrease of $Pr_2(CrO_4)_3$ increased with temperature (Figure 36).

Praseodymium chromite formed in significant amounts during isothermals from 600-680°C, and approximately 1% was detected at 560°C in the period 4-32 hours.

From 600-640°C the initial formation of chromite, in amounts greater than 2%, displayed an increasing rate with time, over a period which shortened with rise in temperature, from 32 hours at 600°C to 4 hours at 640°C. Correspondingly, the period of formation which exhibited a decreasing rate of formation with time, increased with temperature, and at 680°C only this latter behaviour was observed.

In the period 16-32 hours, a deceleratory period in chromite formation for all temperatures except 600°C, the amount of chromite formed decreased as the temperature was raised from 620-680°C. As a result of this at 32 hours for temperatures of 680°C, 640°C and 620°C, the amounts of chromite formed were all within 5%, (figure 37).

There was no exact correlation between the periods in which the rate of formation of chromite increased with time, and the period of decrease of chromate (VI) at each temperature, c.f. chromate (V) decomposition in the La_2O_3-Cr_2O_3 system. The maxima of

chromate (VI) formation were concurrent with the presence of appreciable amounts of chromite.

As previously, the variation in the oxidation state of the unreacted oxide will be described as the variation in the amount of the component oxidation states Pr(III) and Pr(IV).

Within experimental error there was never a significant increase in the amount of Pr(IV), The rate of decrease of the Pr(IV) component diminished with time. This was more conspicuous at higher temperatures because the initial rate increased with temperature in the period 0-4 hours, although the results for 640°C, at 2 and 4 hours were not in the order expected with increase in temperature. In the period 8-32 hours, therefore, the amount of Pr(IV) was almost constant for temperatures between 600 and 680°C, decreasing at most, 5% approximately. It is probable that, since the rate diminishes with time, the greatest rate of decrease in Pr(IV) had occurred within the first hour; also, that the amount decreasing within the first hour of reaction had increased with rise in temperature, for the amount analysed at 1 hour decreased with temperature, (figure 38).

The praseodymium (III) component of the oxide shows an initial tendency to increase, the period in which it increased shortened with rise in temperature. This was, 32 hours at 560°C, but here a minimum value was observed, to be described later, 8 hours at 600°C, 4 hours at 620°C, 2 hours at 630°C, while at 640 and 680°C

it did not increase over any period analysed. The rate of 'formation' of Pr(III) decreased with time, and increased with temperature.

The decrease of the Pr(III) component of the unreacted oxide coincided with the formation of amounts of chromite greater than 2-6°/o. The rate, of decrease, diminished with time, and this was more pronounced at higher temperatures for the initial rate of decrease increased with temperature. Therefore, after 32 hours at temperatures of 620°C, 640°C and 680°C, the amount of Pr(III) present was similar, being approximately 10°/o.

The rates of increase and decrease of Pr(III), both increase with temperature. Therefore the maxima appear at successively shorter times with increase in temperature, after 8 hours at 600°C, to 1 hour at 640 and 680°C. Only 26.36°/o was present after 1 hour reaction at 680°C, with the other maxima falling within the range 28-30°/o, (figure 39).

Praseodymium chromate (V), found only at 560°C, formed with a decrease in rate of formation with time, to a maximum at 4 hours. It then decreased to 2.96°/o after 32 hours. The maximum value of $PrCrO_4$ coincided with a drop in the Pr(III) content of the unreacted oxide where the overall trend between O-32 hours was for the Pr(III) to increase, which it continued to do after 4 hours. The Pr(IV) component of the oxide was apparently unaffected and continued to fall slowly throughout the period O-32 hours, (figure 35).

The rate of formation of the total product decreased with time, with an initial rate of formation which also increased with temperature;

further, the tendency for the rate to decelerate increases with a rise in temperature. Thus the amount of total product which was formed within the first few hours increases with temperature, whereas at 620°C, 640°C and 680°C, at a reaction time of 32 hours, the respective totalswere within about 2°/o of each other, (figure 40).

It was also evident from the isothermals, in addition to the temperature dependence results in air and oxygen, that the decrease in the Pr(IV) component of the unreacted oxide was exactly matched by the increase in the praseodymium content of the chromate(VI) and the Pr(III) component of the oxide, in the absence of significant chromite formation.

FIGURE 19

VARIATION OF PRODUCTS WITH TEMPERATURE, 8h, IN AIR

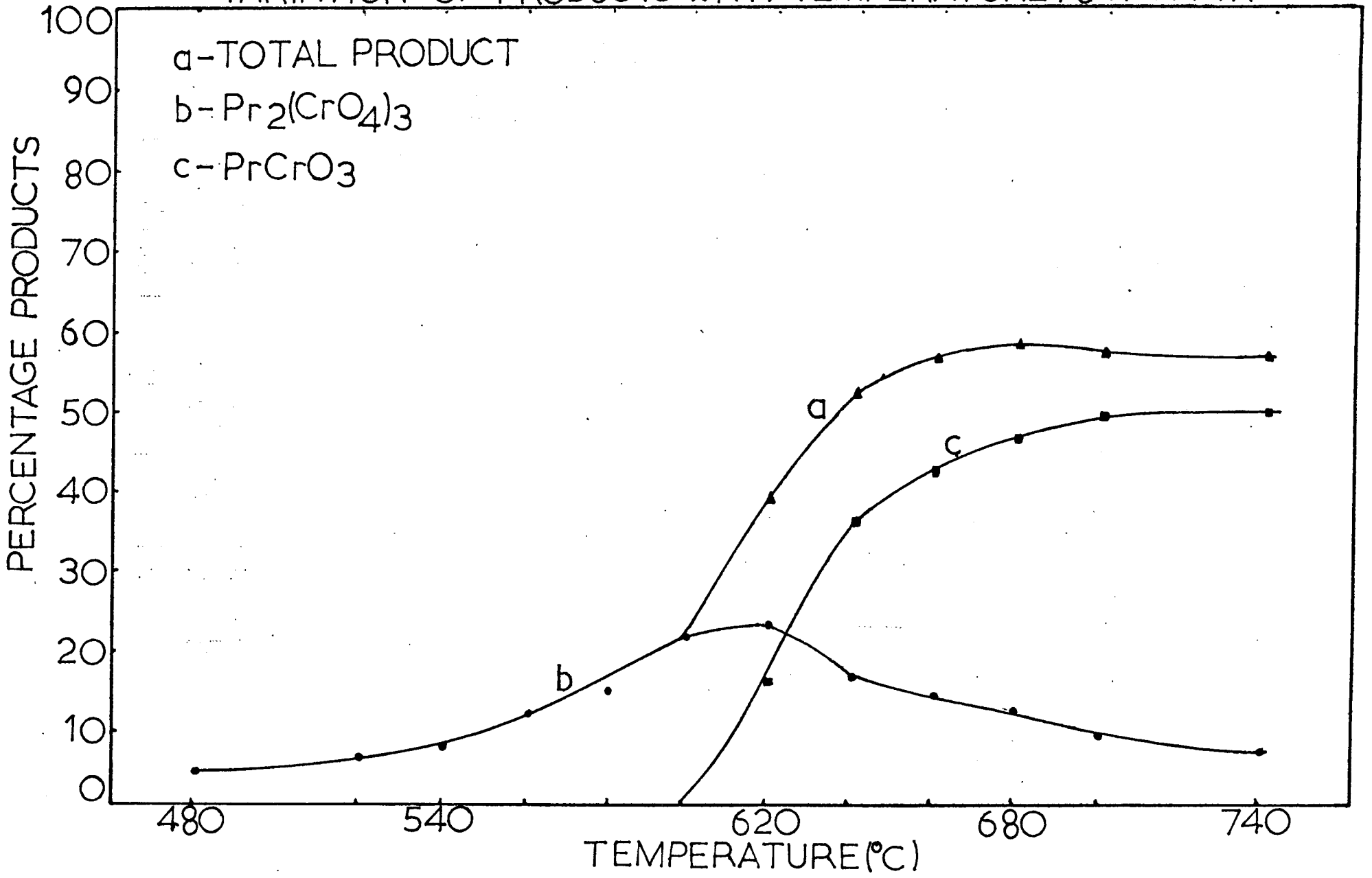


FIGURE 20

VARIATION OF PRODUCTS WITH TEMPERATURE, 8h, IN AIR

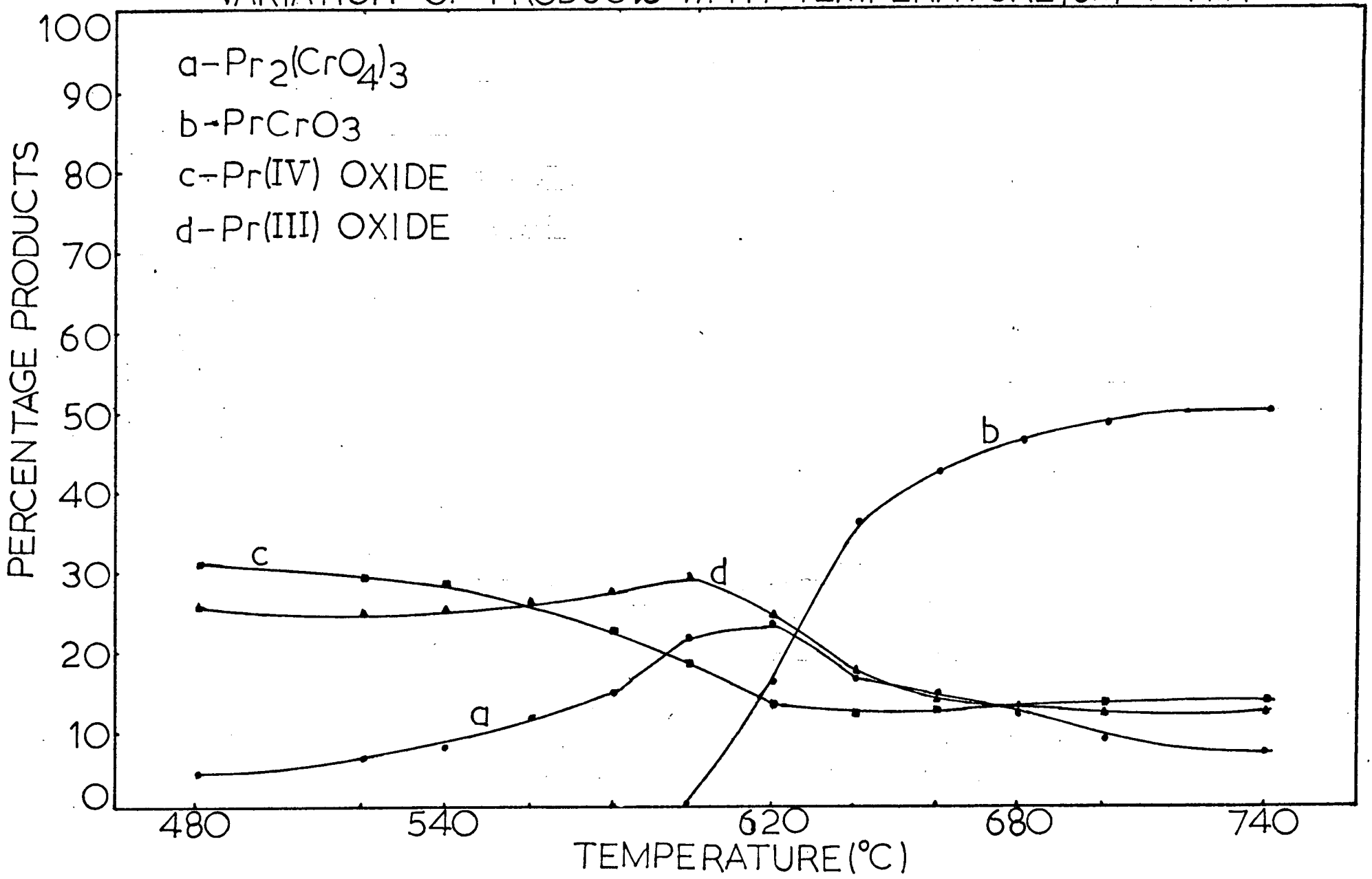


FIGURE 21

VARIATION OF PRODUCTS WITH TEMPERATURE, 8h, IN OXYGEN

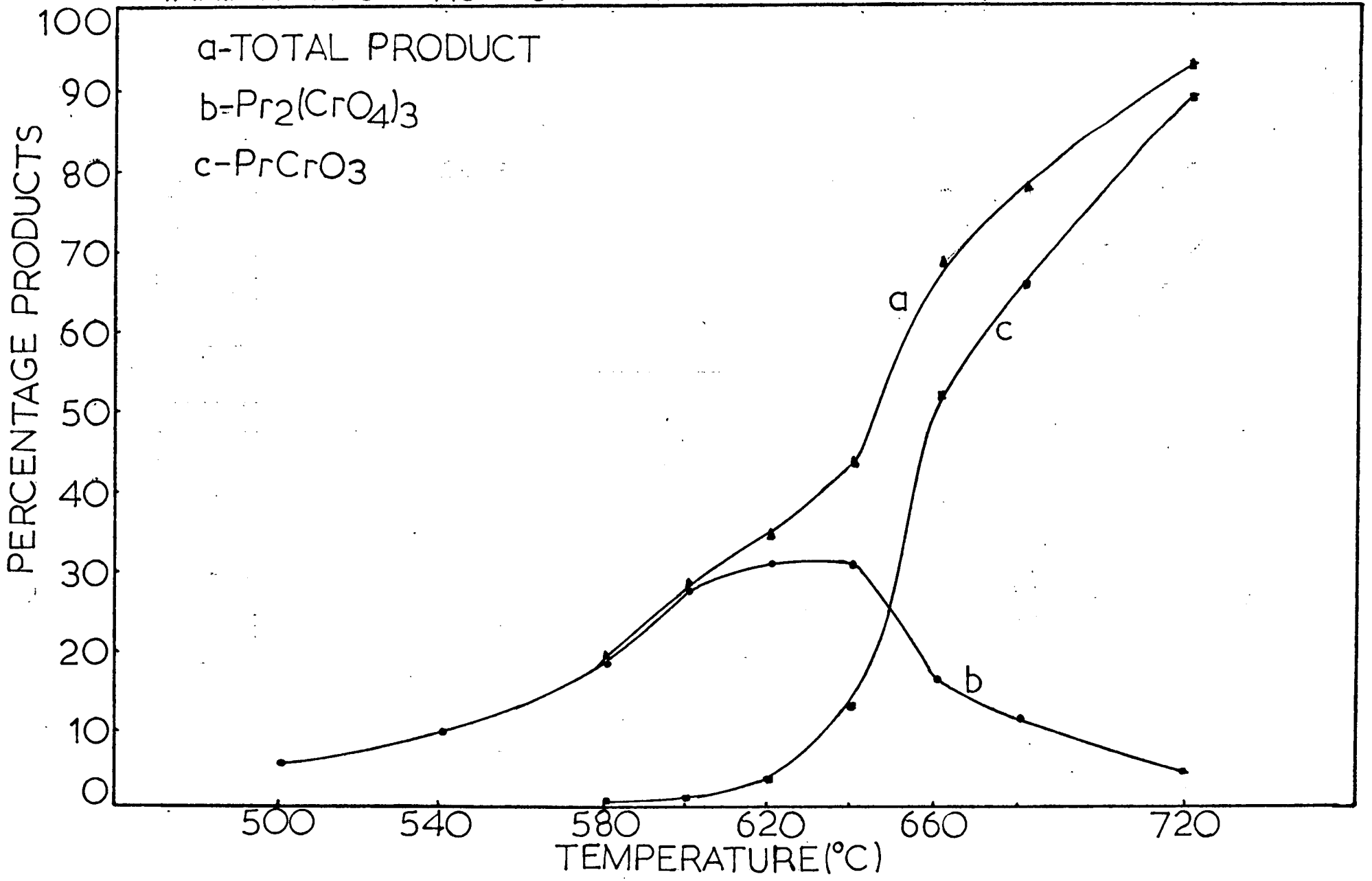


FIGURE 22

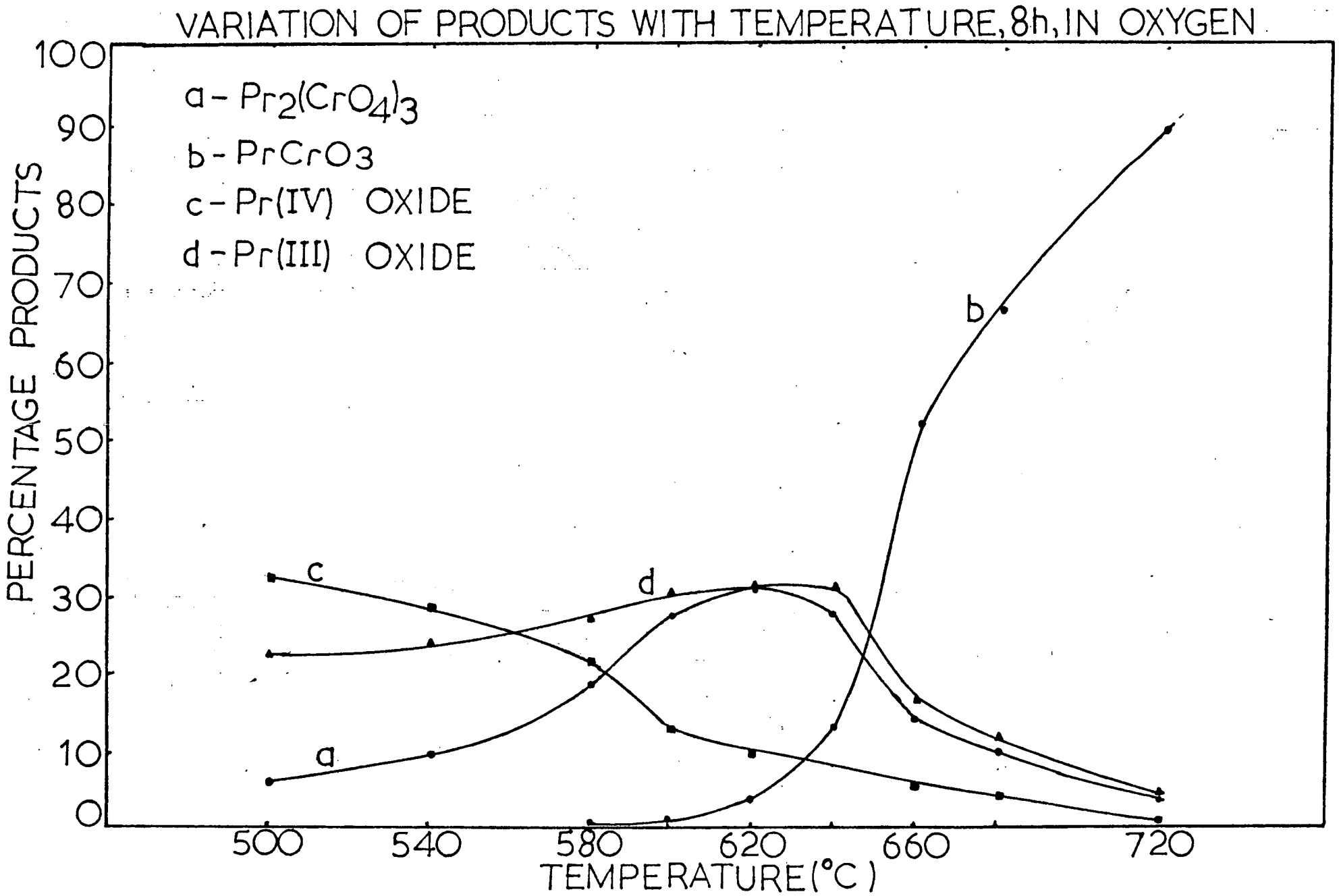

VARIATION OF PRODUCTS WITH TEMPERATURE, 8h, IN OXYGEN
a - $Pr_2(CrO_4)_3$
b - $PrCrO_3$
c - Pr(IV) OXIDE
d - Pr(III) OXIDE
PERCENTAGE PRODUCTS
100
90
80
70
60
50
40
30
20
10
0
500
540
580
620
660
720
TEMPERATURE (°C)
a
b
c
d

FIGURE 23

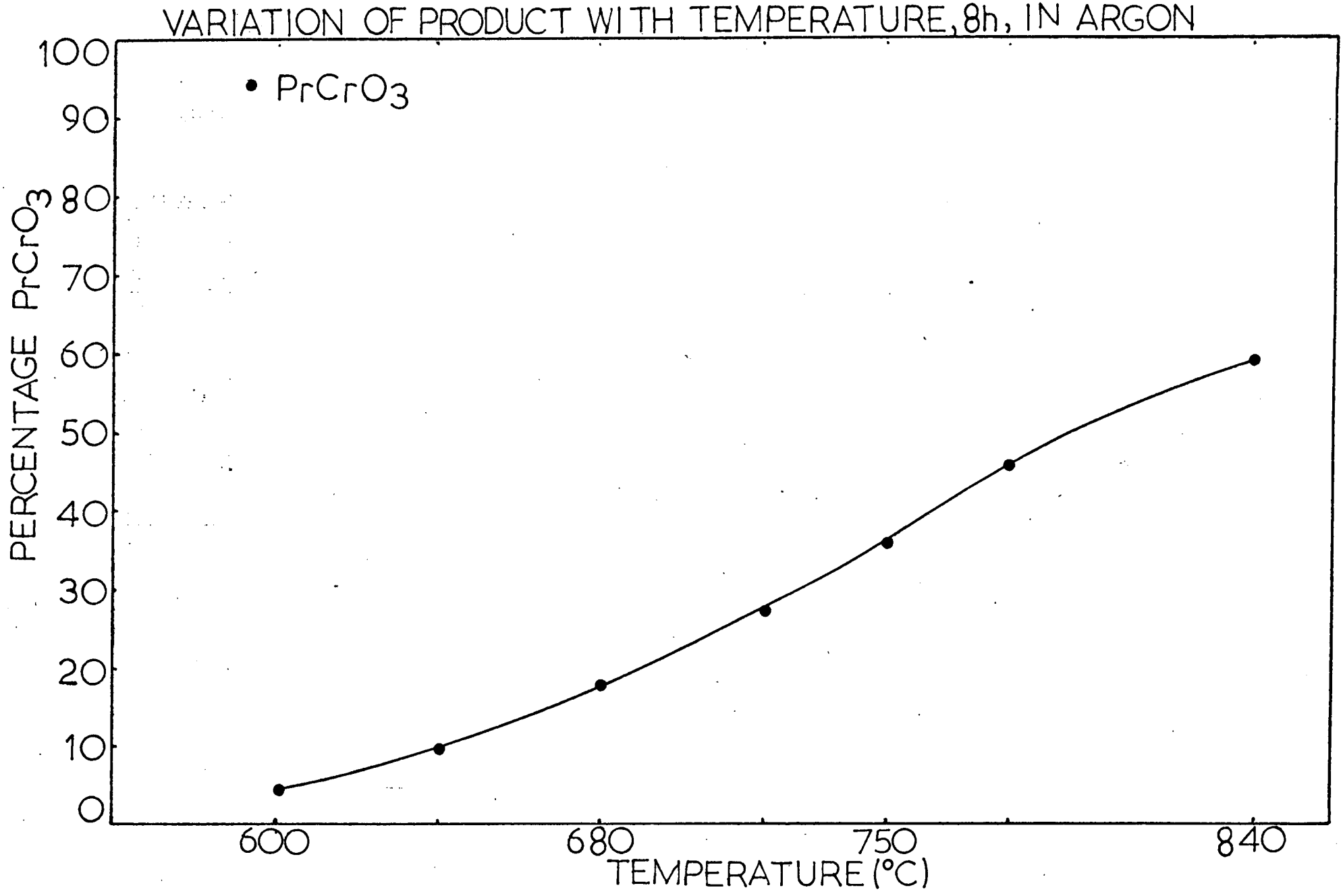

VARIATION OF PRODUCT WITH TEMPERATURE, 8h, IN ARGON
• $PrCrO_3$
PERCENTAGE $PrCrO_3$
100
90
80
70
60
50
40
30
20
10
0
600
680
750
840
TEMPERATURE (°C)

FIGURE 24

VARIATION OF PRODUCTS WITH TIME AT 680°C

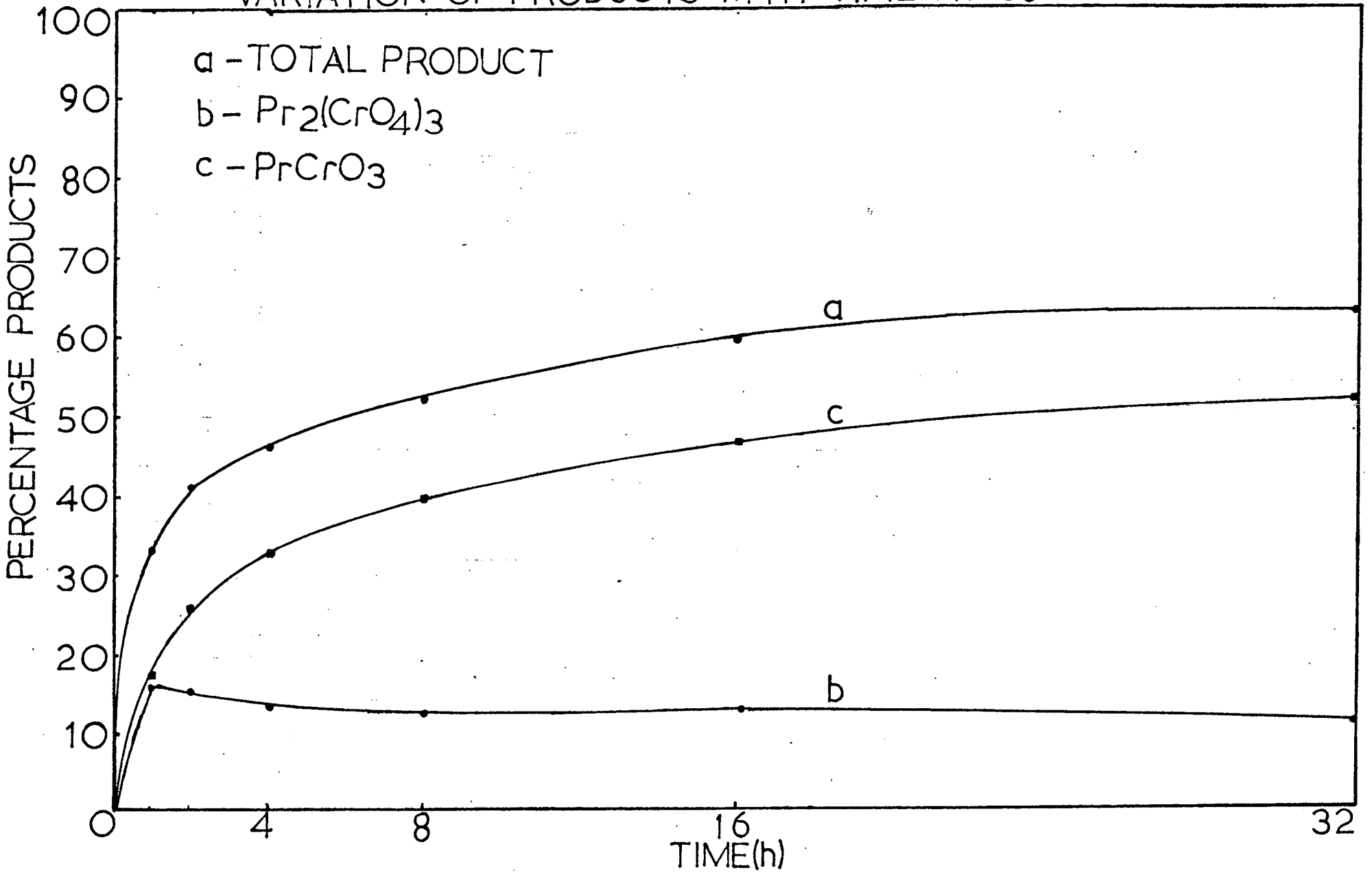


FIGURE 25

VARIATION OF PRODUCTS WITH TIME AT 640°C

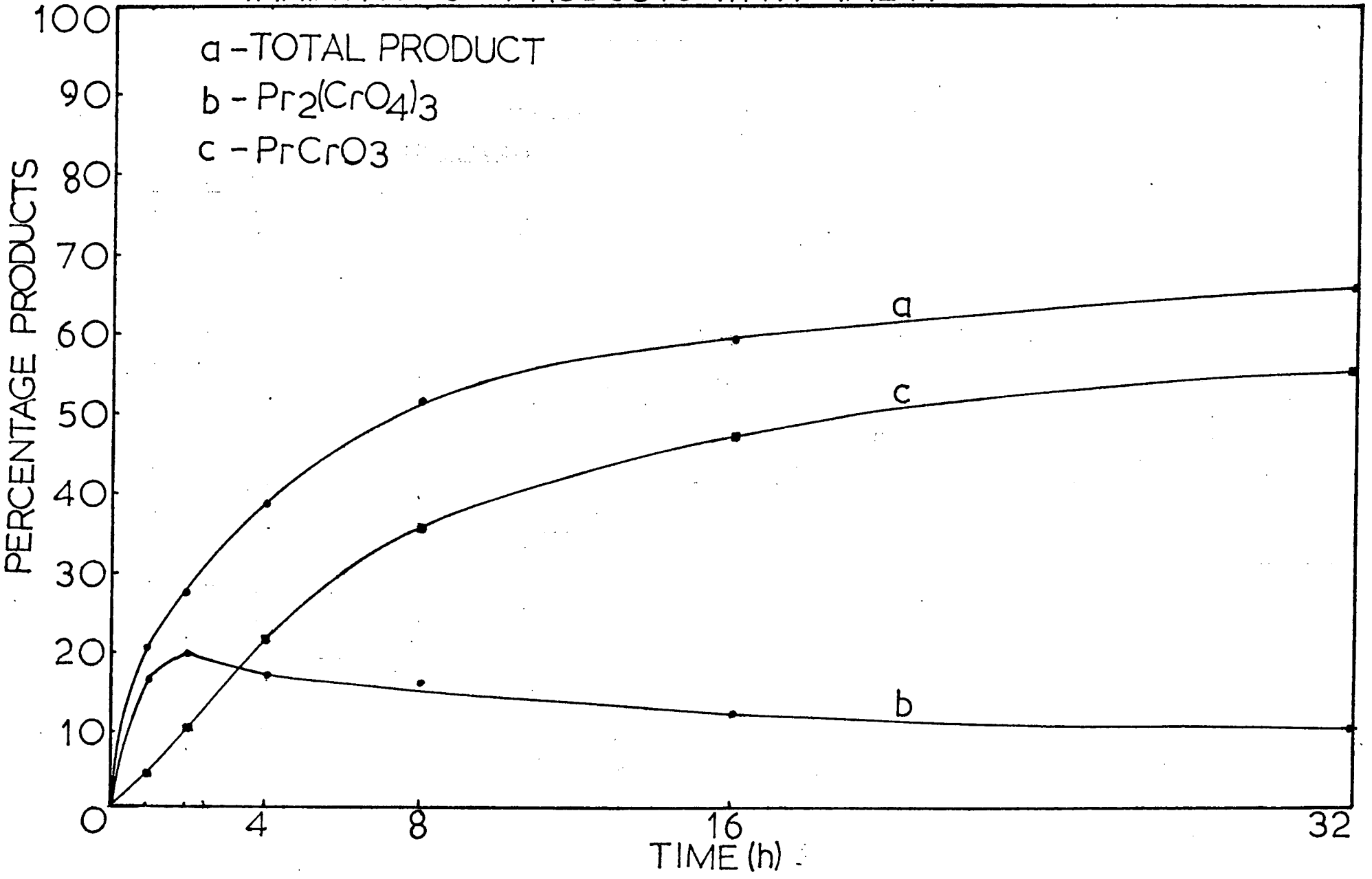


FIGURE 26

VARIATION OF PRODUCTS WITH TIME AT 630°C

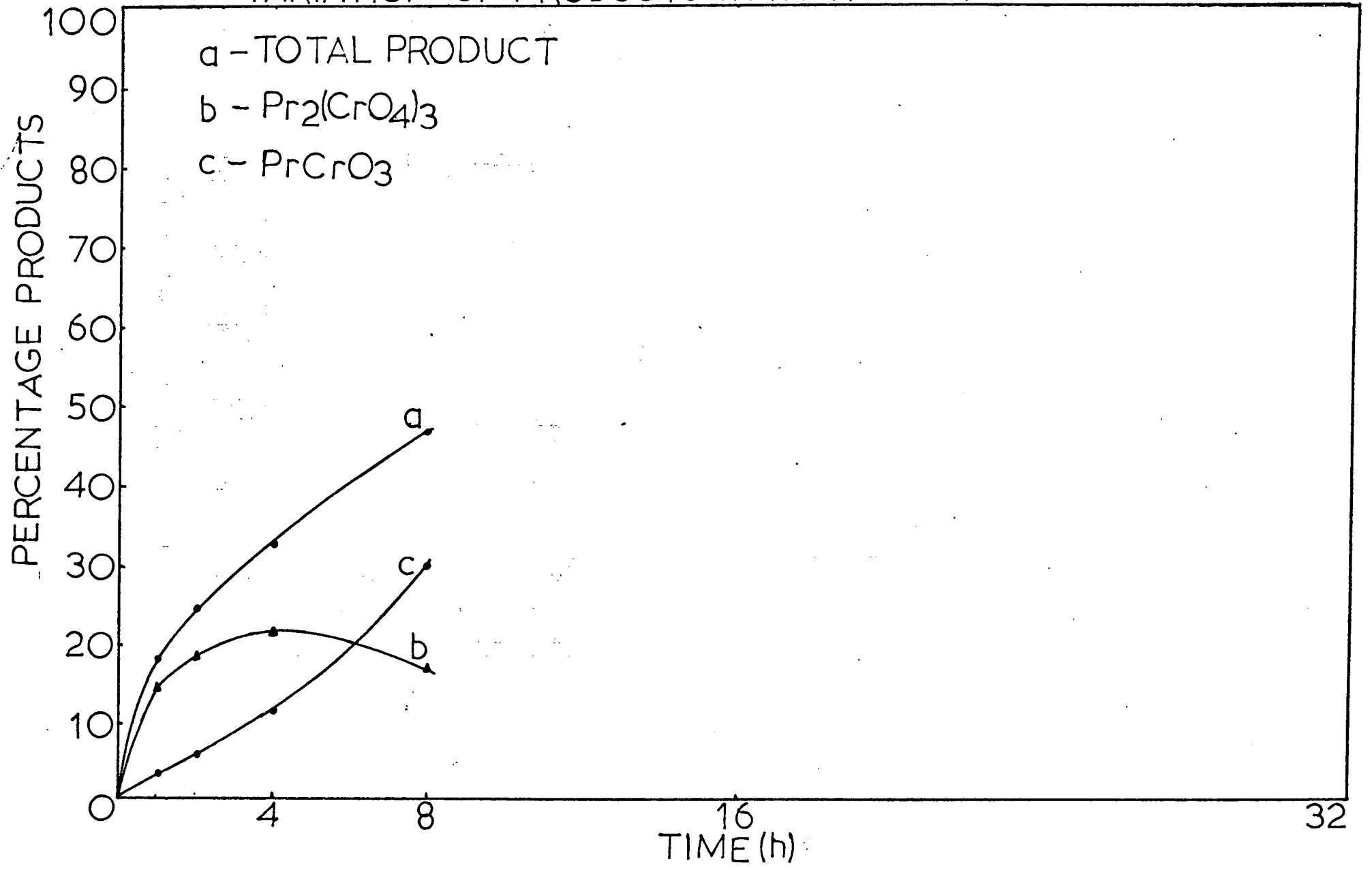


FIGURE 27

VARIATION OF PRODUCTS WITH TIME AT 620°C

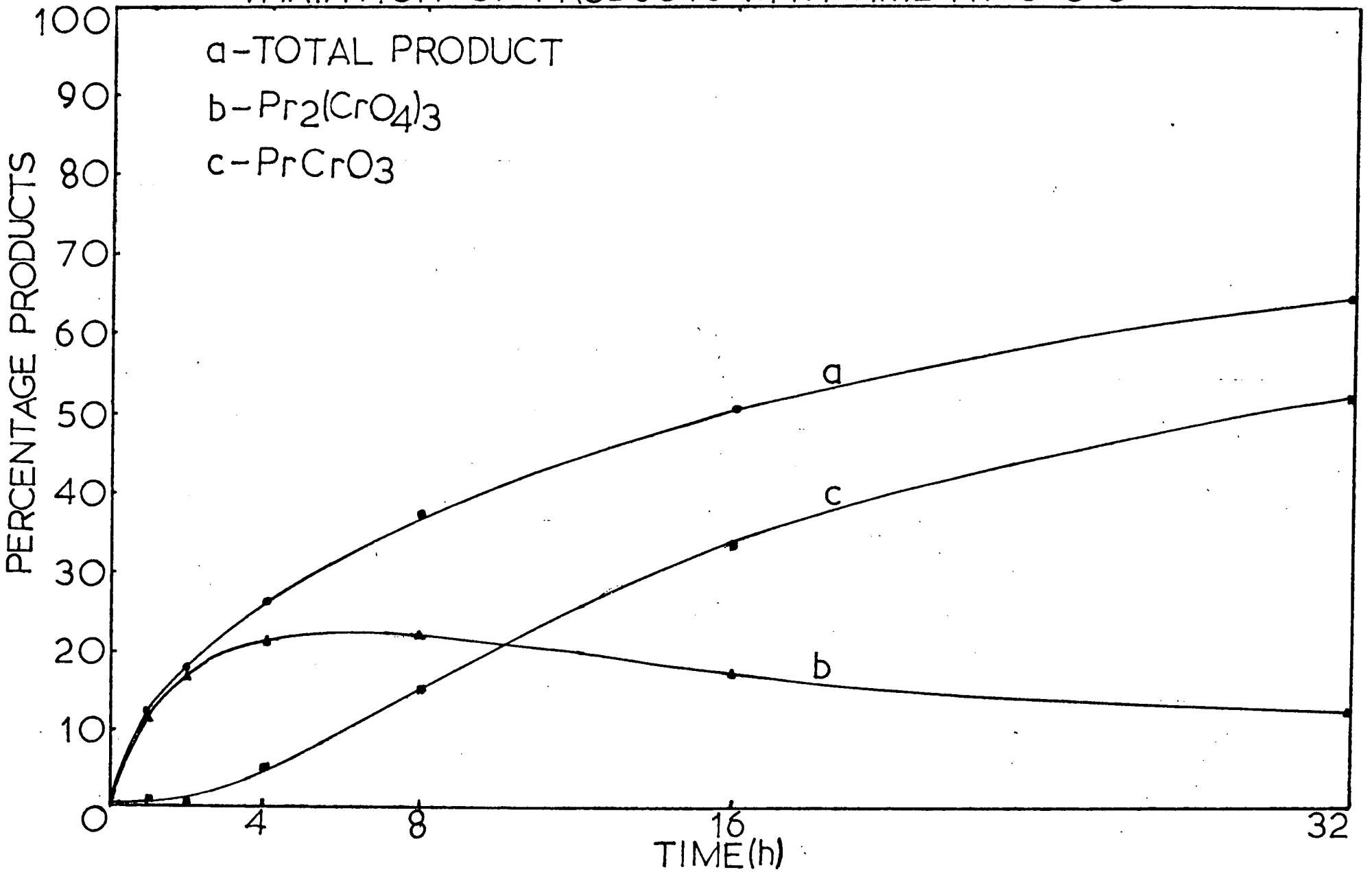


FIGURE 28

VARIATION OF PRODUCTS WITH TIME AT 600°C

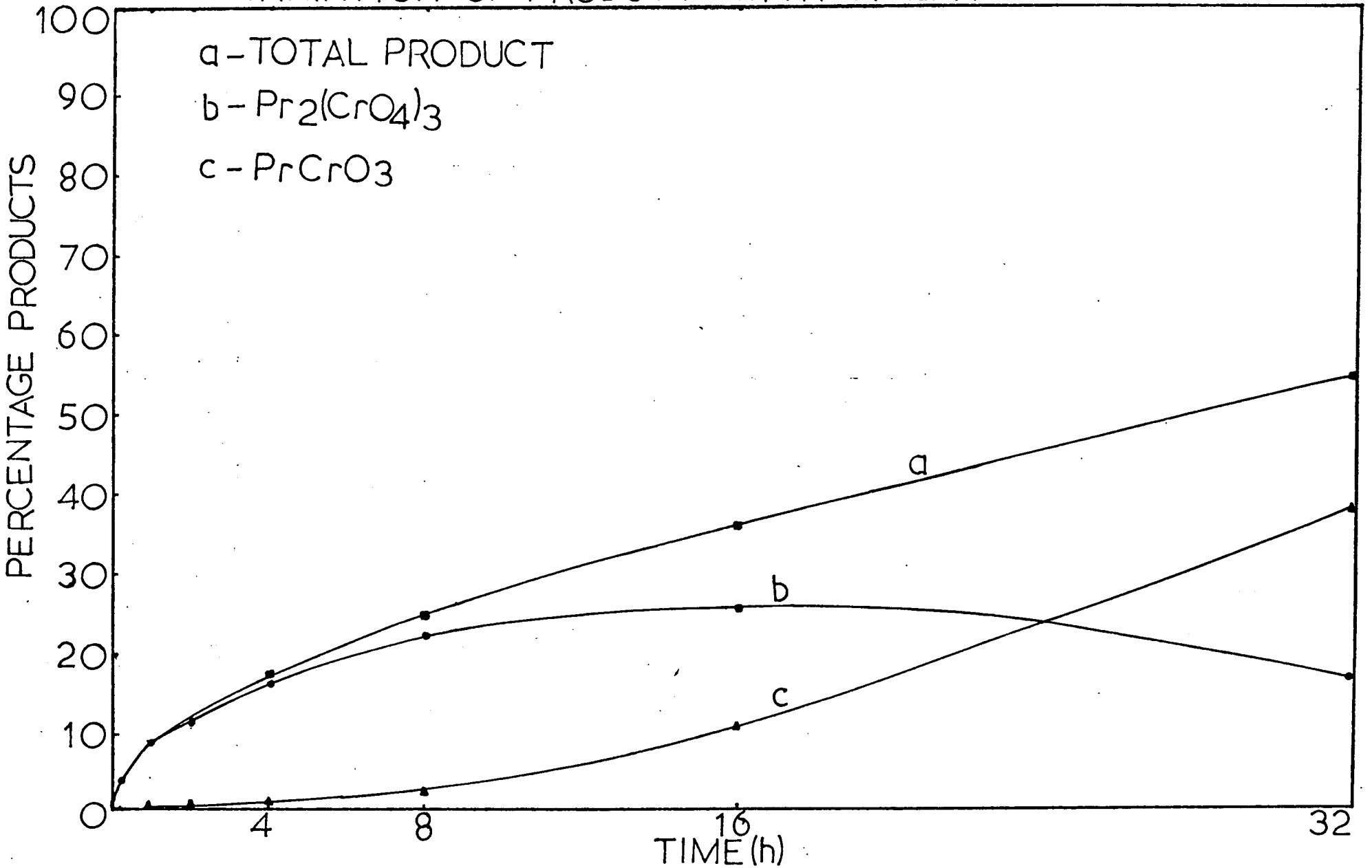


FIGURE 29

VARIATION OF PRODUCTS WITH TIME AT 560 °C

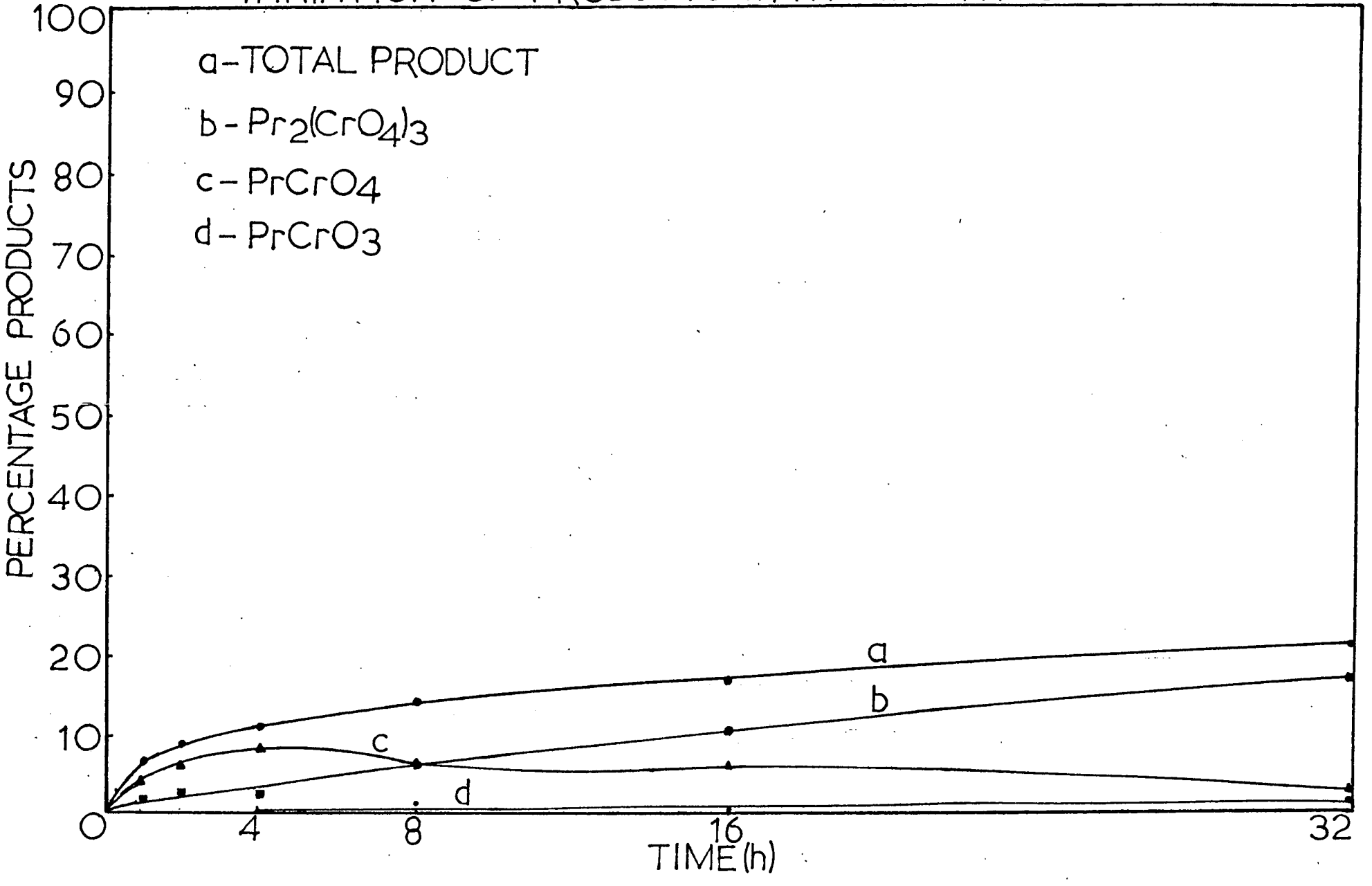


FIGURE 30

VARIATION OF PRODUCTS WITH TIME AT 680°C

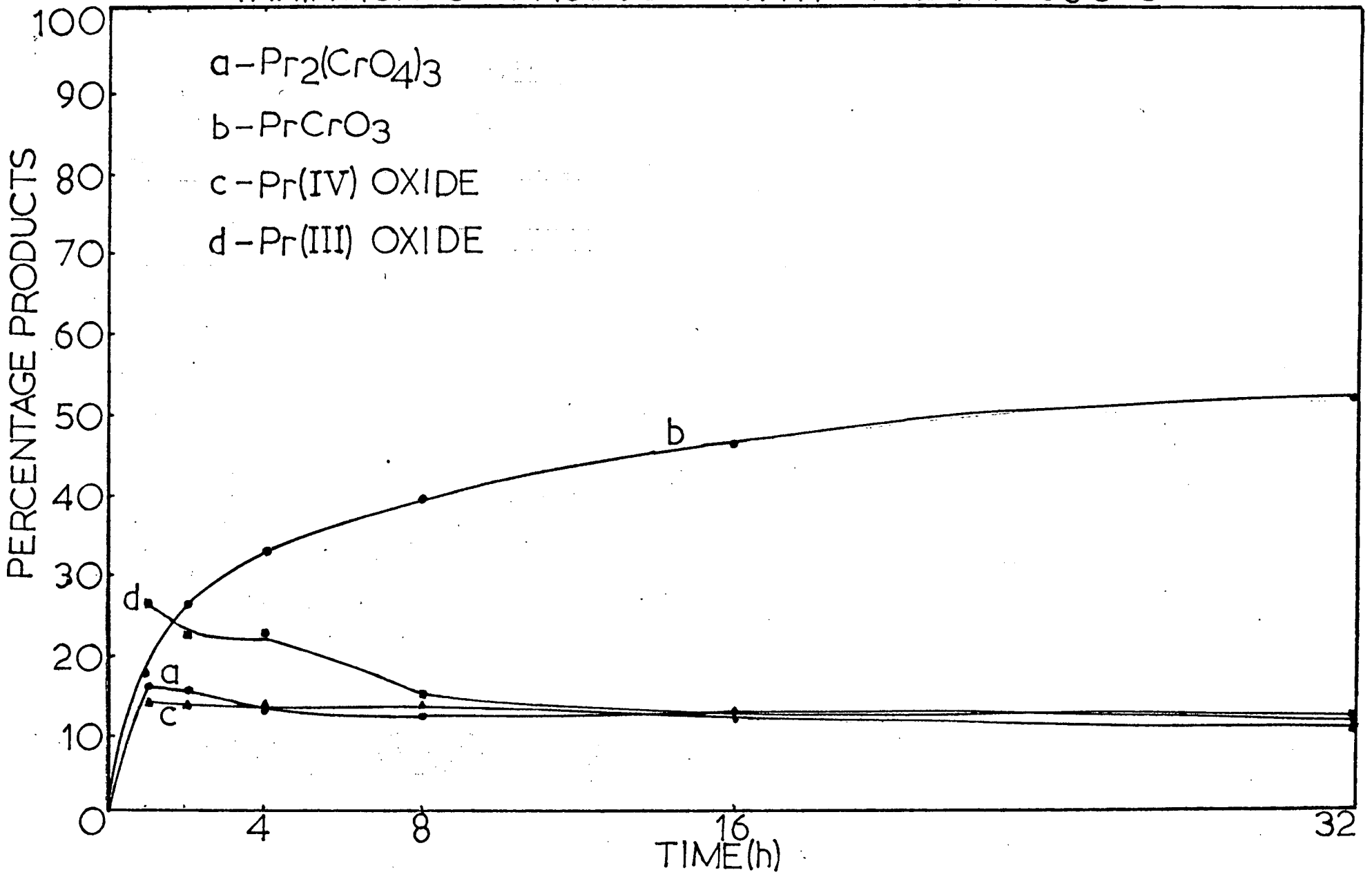


FIGURE 31

VARIATION OF PRODUCTS WITH TIME AT 640 °C

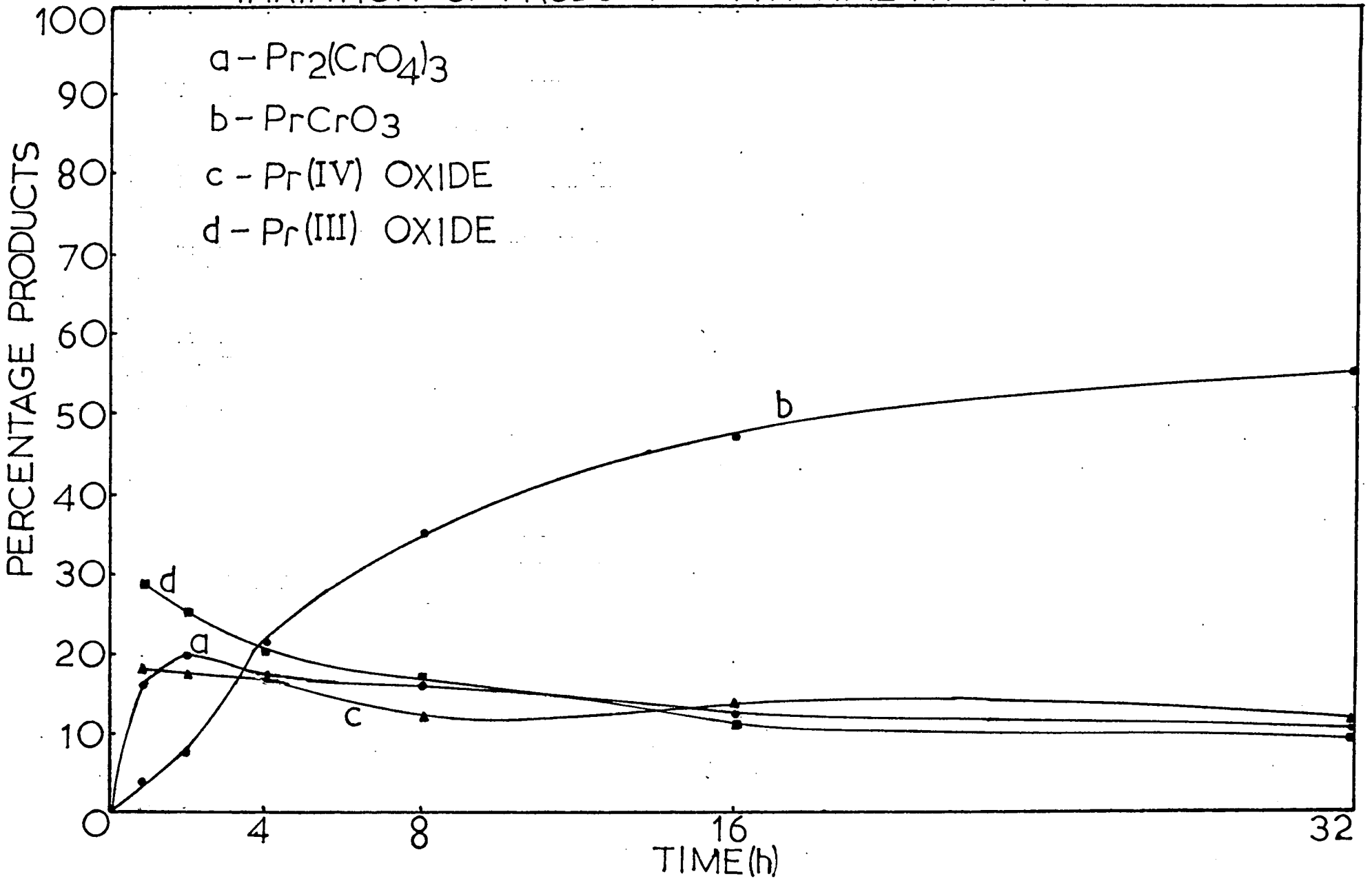


FIGURE 32

VARIATION OF PRODUCTS WITH TIME AT 630 °C

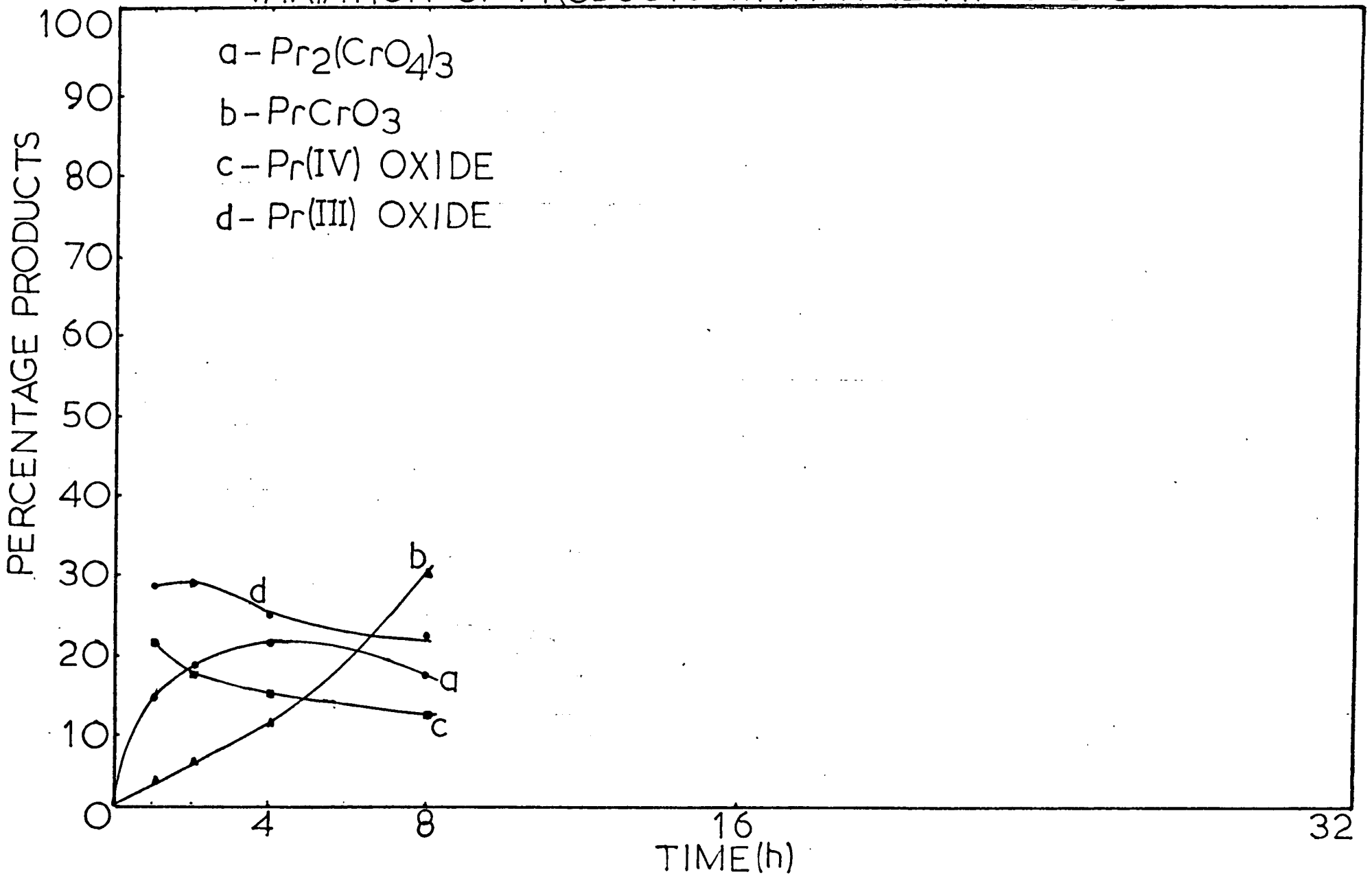


FIGURE 33

VARIATION OF PRODUCTS WITH TIME AT 620°C

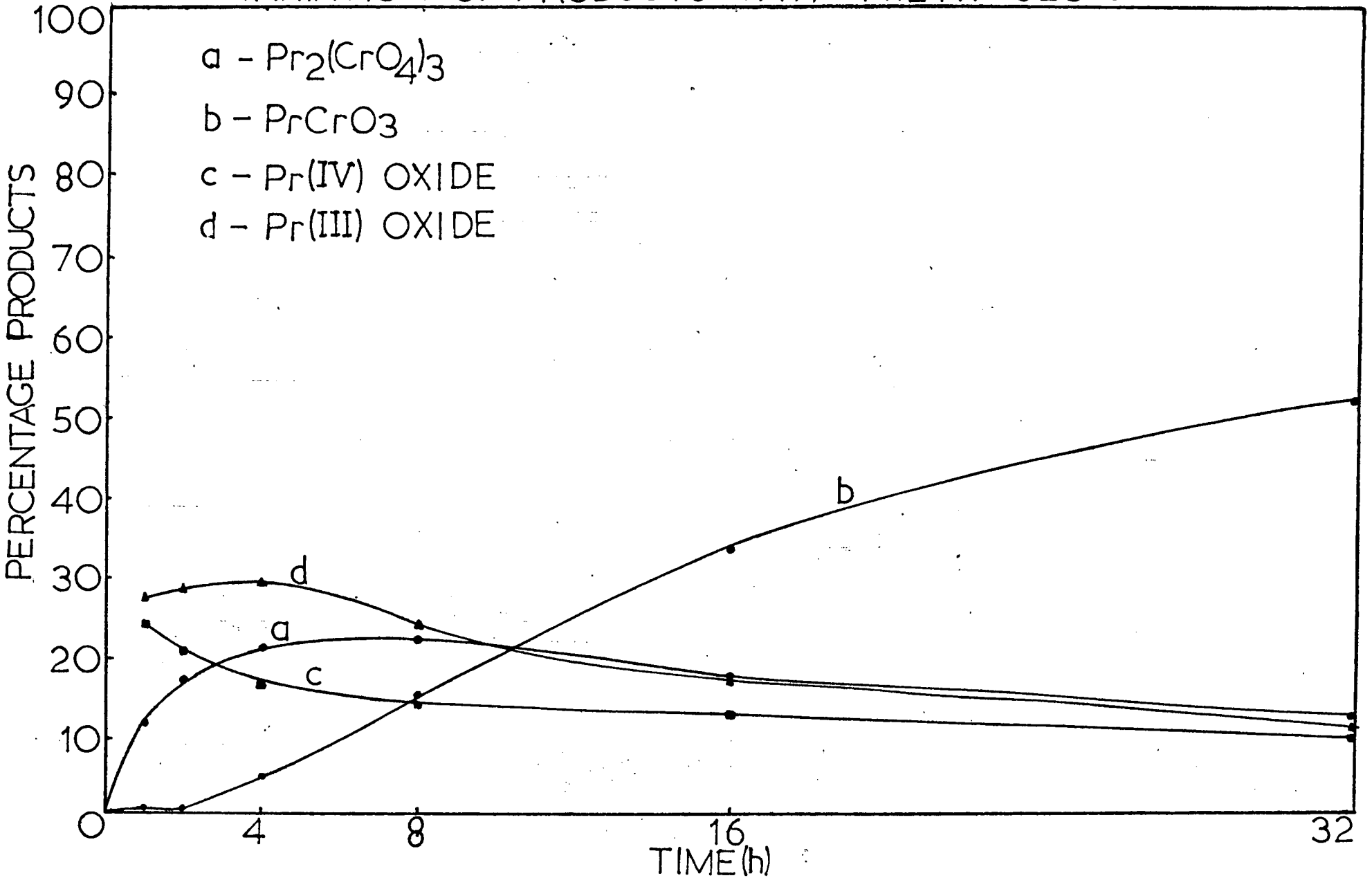


FIGURE 34

VARIATION OF PRODUCTS WITH TIME AT 600°C

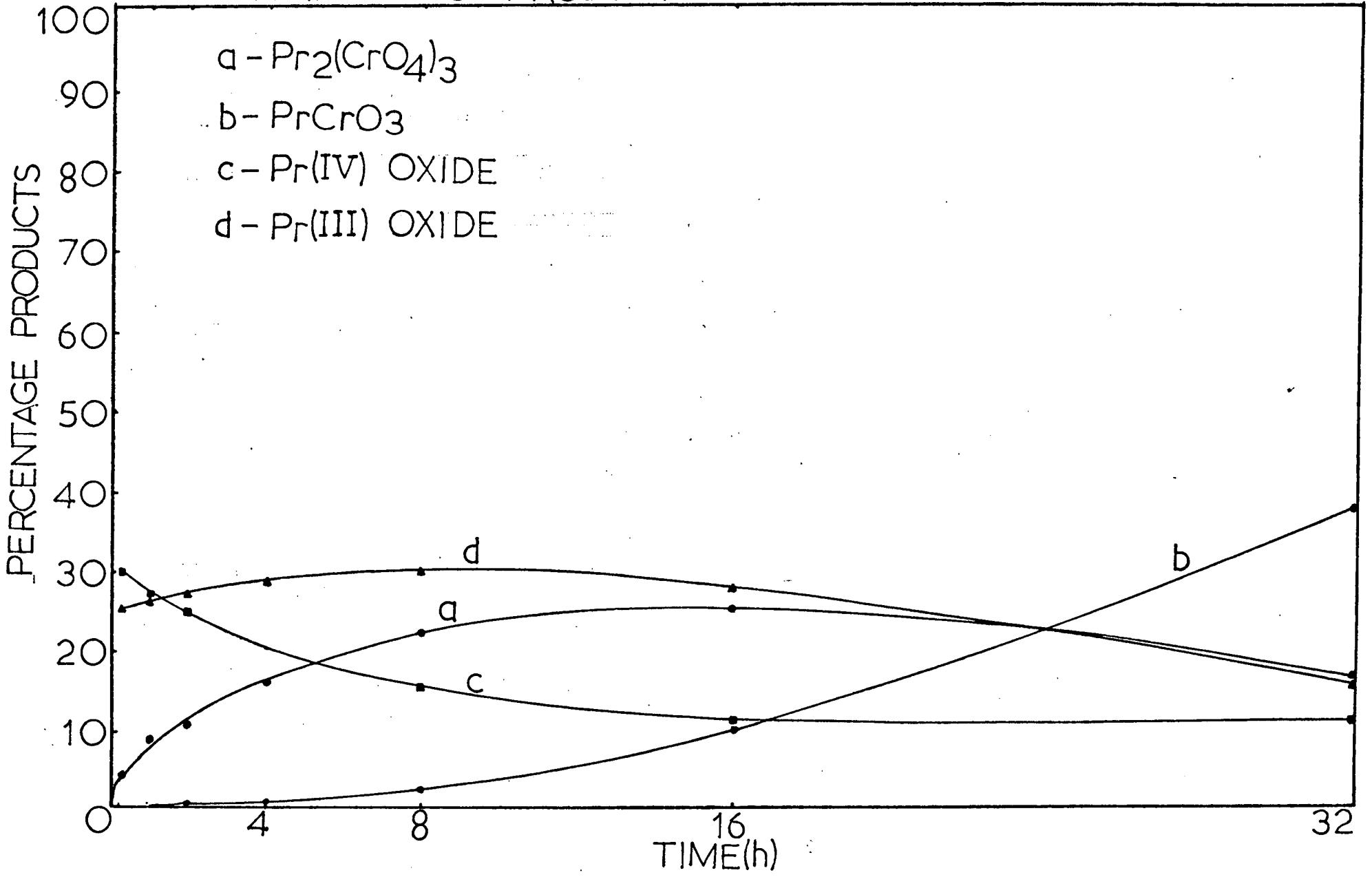


FIGURE 35

VARIATION OF PRODUCTS WITH TIME AT 560 °C

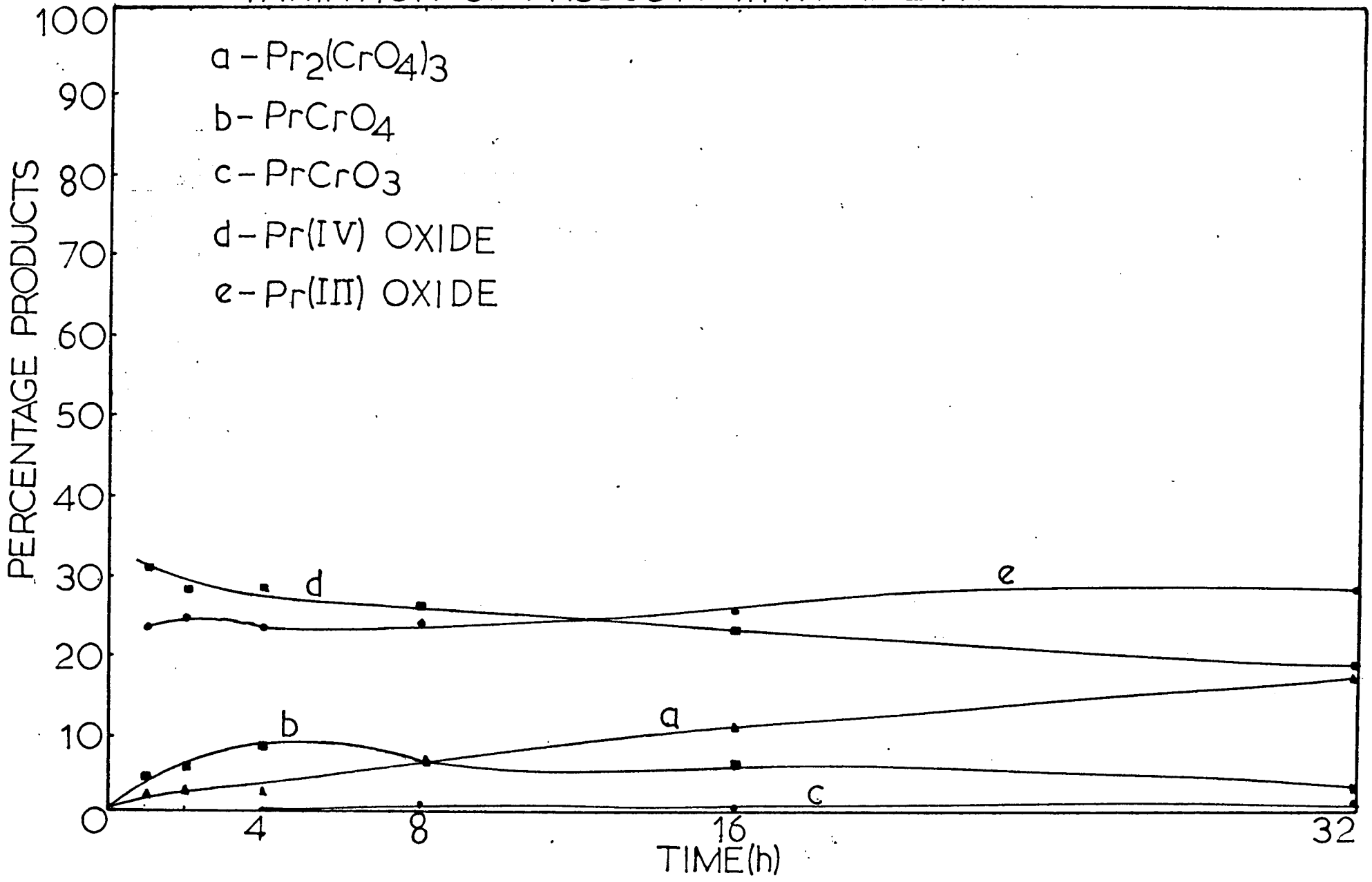


FIGURE 36

ISOTHERMAL VARIATION OF $Pr_2(CrO_4)_3$ (560°-680°C)

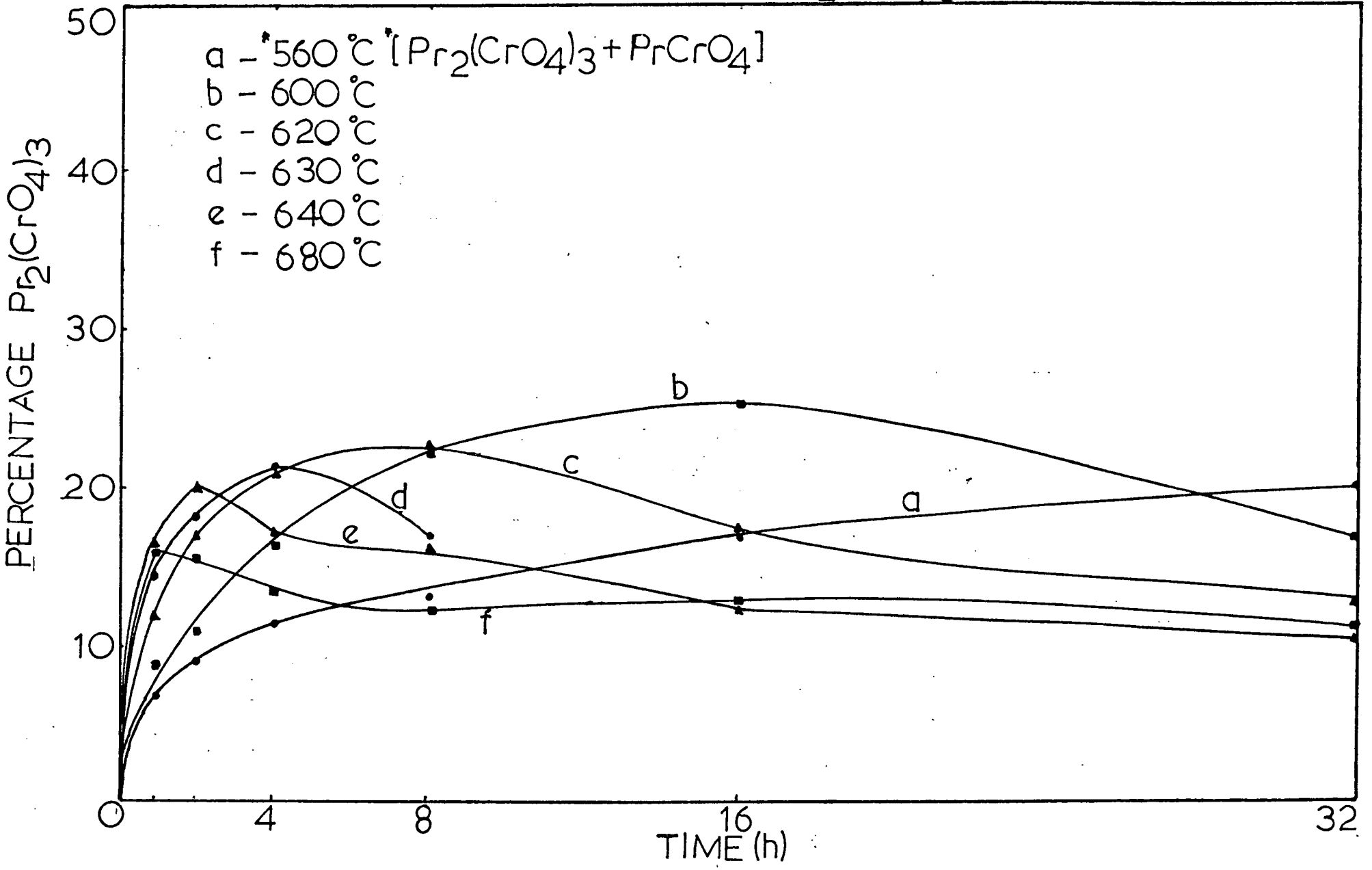


FIGURE 37

ISOTHERMAL VARIATION OF $PrCrO_3$ (600-680°C)

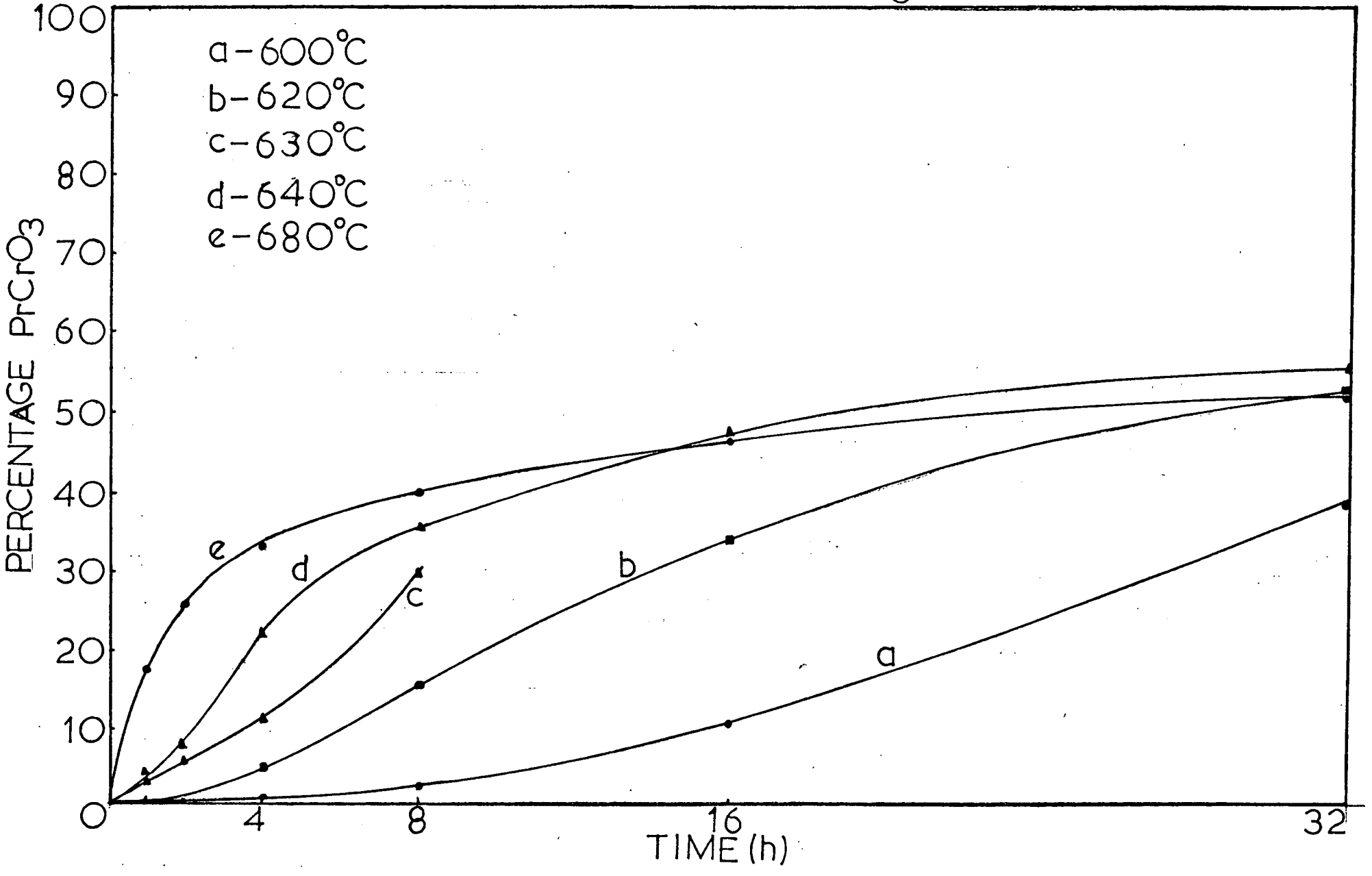


FIGURE 38

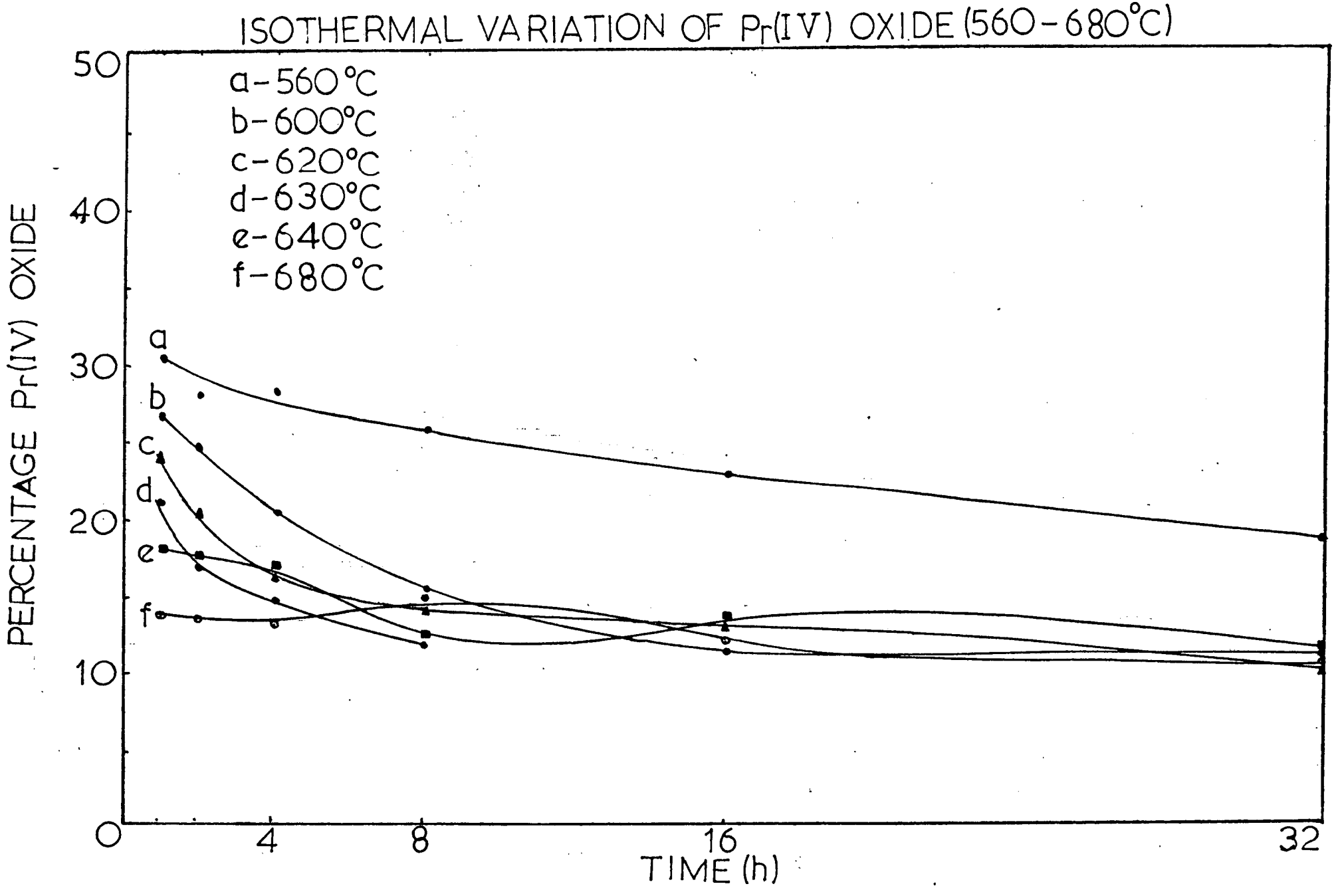

ISOTHERMAL VARIATION OF Pr(IV) OXIDE (560-680°C)
a-560°C
b-600°C
c-620°C
d-630°C
e-640°C
f-680°C
PERCENTAGE Pr(IV) OXIDE
50
40
30
20
10
0
4
8
16
32
TIME (h)

FIGURE 39

ISOTHERMAL VARIATION OF Pr(III) OXIDE (560 - 680°C)

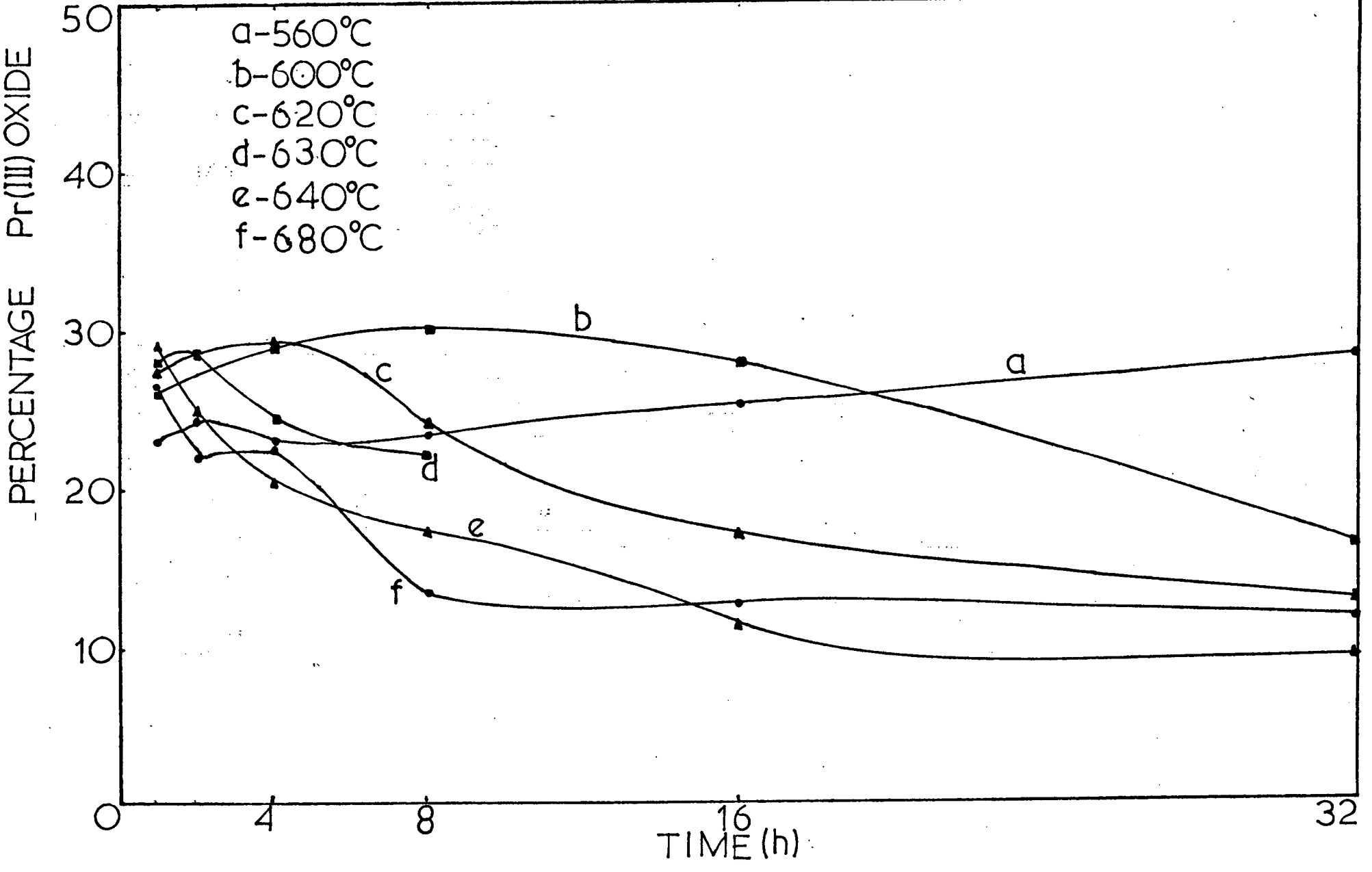
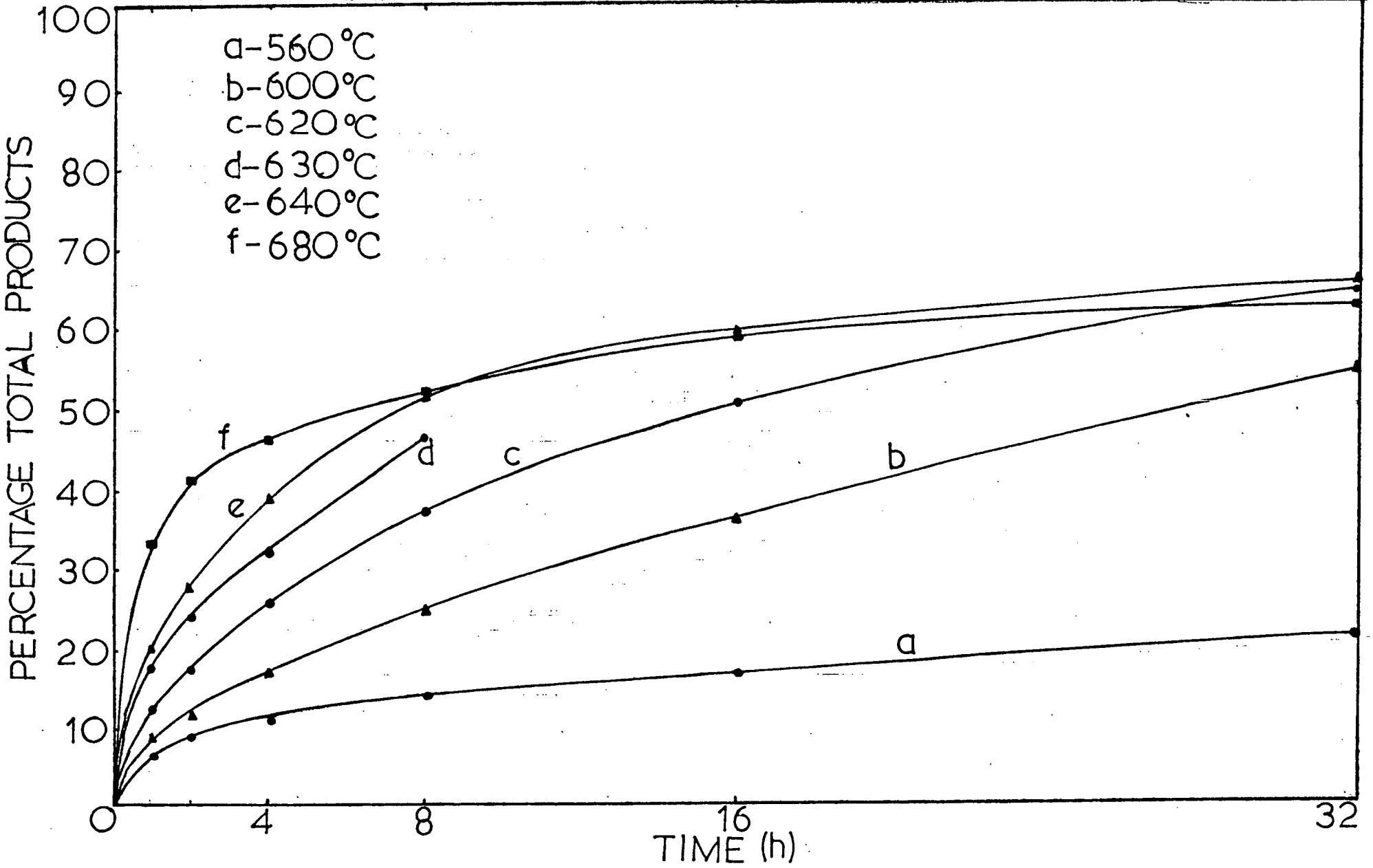


FIGURE 40

ISOTHERMAL VARIATION OF TOTAL PRODUCT (560-680°C)



DISCUSSION

There is perhaps more uncertainty about the mechanisms of reactions in the solid state than about any other branch of chemistry of a comparable length of standing. The problems to a complete understanding have been presented as almost insuperable, e.g. by Welch (1955) and the conclusions derived are often at variance with one another. Of prime importance in the study of solid-state reactions is the determination of intermediate states, which though not necessarily the formation of products, ~~this~~ is predominantly the most significant aspect. In an attempt to understand these states a favoured approach has been to measure quantitatively changes in as many physical properties as possible, as a basis of interpretation of the chemical reactivity. The introduction of powder x-ray diffractometry gave, for a time, new impetus to the examination of product formation in these systems, but its drawbacks were low accuracy with only an ability to record poorly, if at all, initial product formation, which predominantly consists of ill-defined crystallites.

Infra-red spectroscopy and diffuse reflectance spectroscopy do not depend to such an extent on the state of crystallinity of the products, but have other drawbacks including very poor accuracy and uncertainty over assignments, which make their use not completely suitable for the quantitative determination of products.

The approach followed in this work is overwhelmingly a

non-physical one. The phases were identified by chemical analysis, with a fairly high degree of accuracy, facilitated in this case by the three possible products all containing chromium in different oxidation states and with varying chemical properties susceptible to accurate determination by the analysis scheme outlined. It was also feasible to study the changes in the oxidation state of praseodymium oxide during the course of the reaction, and so, throughout the systems investigated all possible chemical transformations whose results were stable during the periods studied could be examined. Obviously, there is a limit to the information obtainable in this way, and this will probably be the purely physical aspects of solid state interactions, e.g. the exact nature of the defect processes which permit diffusion.

Qualitatively at least, those factors which affect the reactivity in the solid state have been identified and their effects examined. These factors can be broadly classified into two groups:-

1) Factors which alter the reactivity but do not control the rate (mainly structure sensitive)

2) Rate determining factors (mainly structure insensitive). This is in some ways an artificial distinction since there is doubtless some degree of overlap between the two for chemical reactivity is both structure sensitive and insensitive. Hence the morphology of the system must be taken into account in any description of the mechanism. The factors in group 1) do not easily admit of proper kinetic investigation and therefore must, as far as possible, be

standardised. They include the distribution of size and shape of crystallites, intimacy of contact, method of preparation, subsequent mechanical treatment and thermal prehistory including sintering. The size and shape of crystallites determine the area of the surfaces of reactants in contact and this is of fundamental importance in determining the reactivity. The surface of a crystallite is the region of highest energy and it contains the largest number of imperfections, mainly dislocations. It is thus the most reactive, and the most likely area for incipient reaction to occur since there is an interface in contacting crystallites or an interface capable of being generated on the surface, e.g. by surface or gaseous diffusion of one reactant to the surface of the other.

The method of preparation of the reactant(s) can markedly affect the reactivity by producing a greater degree of imperfection in the crystallite and by altering the average particle size, although these effects can to some extent be eliminated by sintering at a uniform temperature. That intimacy of contact can radically alter the reactivity is exemplified by the co-precipitation of reactants showing very different reactivity from mechanically ground crystallites.

The most notable change in reactivity produced by such factors, in the systems studied, was that in the La_2O_3-Cr_2O_3 system when a new supply of chromic oxide was used, despite identical pretreatment. The changed condition of the Cr_2O_3 was

shown physically by a change in colour of the mixture and chemically by a reduced overall reactivity, with an increase in the formation of chromate (VI) and a decrease in that of chromate (V).

The overall rate of reaction will be governed by:-

1) The extent, speed and nature of the phase boundary processes, which may include,

a) The transference of material from one phase to another.

b) Chemical reaction.

c) Formation of nuclei and growth of reaction product, or a combination of all three.

2) Diffusion through the product layer.

3) A morphology factor, defined as 'the spatial and temporal sequence in which all possible products can occur', (Cohn, 1948).

There is no need at this stage to elaborate on any of the points enumerated above, but a few general comments on the diffusion process may be appropriate for this appears to be of paramount importance. Both chemical reactivity in solids and the mechanics of the diffusion process are intimately bound with ideas on the defects which occur in crystals. It is possible to classify types of defect solid which include the following: true deviations from stoichiometry, deviations caused by impurities of one type or another and dual valency semi-conductors, e.g. Pr_6O_{11}, but innate imperfections in crystals are commonly thought to be of two main

types (a) Point defects and (b) Dislocations. Point defects are structure insensitive and the two principal types, Frenkel and Schottky, have been used to explain bulk cationic diffusion in ionic solids. These types of defect consist mainly of missing or misplaced ions, and at any given temperature these defects are in equilibrium with the rest of the lattice. Dislocations are structure insensitive, and there are two main types, edge and screw. They are thought responsible for increased reactivity at grain boundaries or internal surfaces, the dislocation lines affording relatively easy diffusion channels. It is further believed, that low temperature diffusion is mainly confined to surfaces or grain boundaries; while, true bulk diffusion requires a higher activation energy, associated with the Tammann temperature, and is believed to be the only process capable of producing appreciable reactivity between solids.

Both point defects and dislocations can be found in well formed crystal structures, although the crystal structures of incipiently formed product, particularly at low temperatures, are poorly defined and are likely to be more highly defective.

Although the diffusing species has hardly ever been conclusively identified in reactions between solids there is evidence which suggests diffusion of molecular species: this, to account for the extremely low ionic mobility observed during reaction. In systems involving Cr_2O_3, CrO_3 has frequency been cited as a diffusing entity, although only in the gas phase or along surfaces.

The results obtained for the systems studied here are complex; it is therefore desirable before discussing them to describe, as a means of clarification, known types of solid state reactions believed to operate in these systems. These are as follows:-

1) Oxidation of a complex oxide system, PrO_x.

2) Surface oxidation of one reactant into the gas phase.

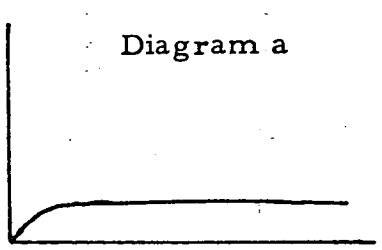
3) Solid + Gas reaction.

4) Decomposition, Solid → Solid + Gas.

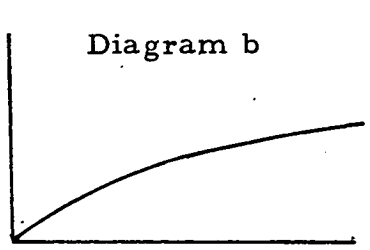
5) Solid + Solid.

Reactions 1) and 2) will be considered when the Pr_2O_3-Cr_2O_3 system is discussed, while the more general reaction types discernable in these systems are now described, for they give rise to typical kinetic plots similar to those found in the systems studied.

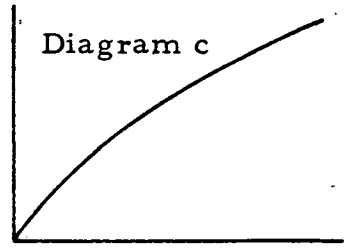
In the reactions of solids and gases of major concern is the formation of a product layer over all surfaces or over the surface of one of the reactants. There are two extremes of kinetic behaviour possible, a linear rate law, never observed in these systems, and protective product formation, where the product layer covering the surface permits little diffusion. There are modifications of this extreme, in varying degrees dependent on the amount of diffusion possible through the product layer. These are all shown below in diagrams a-c.



limiting law



logarithmic law

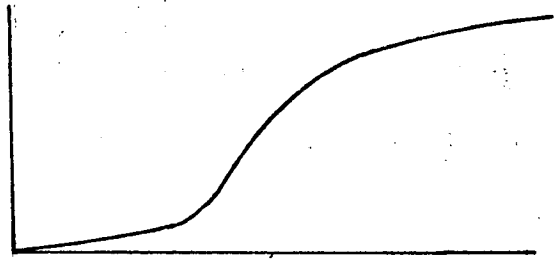


parabolic law

It is often difficult to derive equations for the kinetics of solid state reactions, but using a simplified model for reactions between crystallites, Janders obtained the following equation for solid + gas interactions of a parabolic type, $[1-(1-\alpha)^{1/3}]^2 = kt$, where α is the extent of reaction at time t.

The decomposition of solids can show a variety of kinetics, the most common giving rise to the sigmoidal shape of curve, diag. d.

Diag. d.



The initial stage can be understood as nucleation, i.e. the formation of small amounts of solid product, which as they grow produce a more extensive reactant/product interface thus accelerating (2nd. stage) in a cooperative manner the rate of formation of new solid product. The deceleratory phase of the reaction is encountered as the nuclei begin to overlap with subsequent decrease in the reactant/product interface (Galwey, 1967).

For the pure solid-solid interaction, without interference of a gaseous phase, it is difficult to construct a coherent kinetic model. Reaction is most likely to occur at the region of contact

between the reactants and diffusion of one or more reactants is then necessary for further reaction to take place. As already stated there may be evidence for the diffusion of molecular species capable of, initially, free orientation. Certainly Rubinchik (1973) in applying the Janders equation to the formation of $NdCrO_3$ in vacuo and achieving a fit with this equation would seem to suggest that the rate determining step was the diffusion of gaseous species through the chromite product layer.

One of the most striking results that accurate quantitative determination of products in the solid state has revealed for the systems Ln_2O_3-Cr_2O_3 is that an order of reactivity exists in these systems. This was evident from the work undertaken here, on the systems Ln = La Pr, Y and that of Gibb (1973) for the system Ln = Nd. This was confirmed for the systems Ln = Sm, Gd by Campbell (1975). It must be emphasised that this is a general order of reactivity, ignoring for the moment the nature of the products, which is considered later.

It is manifest that the reactivities of the systems Ln_2O_3-Cr_2O_3, Ln = La, Pr are greater than that for Ln = Y. A comparison of the systems Ln = La and Pr should be approached more cautiously. Most of the reactions in the lanthanum system used a more reactive chromic oxide than that subsequently used in the Ln = Pr and Y systems, but the ~~more~~ less reactive chromic oxide was also used in several reactions in the lanthanum system. A comparison

of the total product in the two systems for a temperature dependence in oxygen over approximately the same temperature range would indicate a similar general reactivity. The praseodymium system is possibly more reactive than it might otherwise have been because the praseodymium (III) oxide was not pre-calcined at 900°C for 4 hours, unlike lanthanum and yttrium (III) oxides. The results of Gibb (1973) show that the reactivity of the Nd_2O_3 system is less than that of the Pr_2O_3 system. Thus a tentative reactivity series would be:- La > Pr > Nd > Y. There are good reasons for believing that the differences between the systems are not due to structure sensitive factors such as size, shape, etc. Similar pretreatment and preparation of mixtures was extended to all of these systems and random variations in these quantities could not explain the regular progression observed, which is in the order of the lanthanide (III) ion radii.

The decrease in reactivity must in some way be associated with the properties of the lanthanide (III) ion. It is of interest to ascertain the processes which are likely to be rate determining. These could either be related to the phase boundary processes or to diffusion. The nature of the phase boundary processes are likely to differ in an argon atmosphere compared with one containing oxygen, but the trend La → Y is apparent, whether the atmosphere be air, oxygen or argon. Although the diffusion process may also be altered in different atmospheres, the parabolic shape of the curve in argon

indicates that the reaction is diffusion controlled. Structural considerations alone support diffusion control for (Stone and Tilley, 1972) have argued that in perovskite structures, such as the lanthanide chromites, which are the only product formed in argon, ~~that~~ the movement of the smaller cation Cr^{3+} through the lattice would be difficult, and therefore diffusion through this lattice during synthesis of pervoskite would be slow. In the Y_2O_3-Cr_2O_3 system where the amount of chromate formed is small the results can be satisfactorily explained by either a fast initial reaction and a very slow diffusion process or, by a fast initial reaction with a relatively rapid diffusion process and a slow subsequent rate of reaction, which is unlikely. Many reactions in these systems studied can readily be explained by diffusion control in the later stages of reaction where high yields have been obtained, as the difficulty encountered by one or more reactant species in progressing through a thick product layer, to reach the phase boundary and so form new products, as they give rise to parabolic kinetic plots.

The other approach is to ask what are the properties of the lanthanide ion which could influence the reactivity in these systems. One property is the size of the ionic radii and the only other of significance is the electronic configuration. The latter reason seems unlikely because it does not offer an explanation of the gradation observed. The electronic energy states of solids containing these ions as obtained from absorption spectra do not

provide evidence to suggest a correlation between this and reactivity. It would therefore seem to depend on the radii of the Ln(III) ion. The reactivity is observed to increase as the size of the Ln(III) ion increases; it therefore seems unlikely that the diffusing species is Ln(III) or contains this ion, because increase in size of the mobile species would hinder diffusion. Indeed, evidence later in the text supports the diffusion of a chromium containing species.

The order of reactivity may be due to a crystal structure related phenomenon, but there are too many unknowns to provide an explanation. As a convenient rationalisation of the results it is suggested that the overall reactivity is controlled by a structure insensitive diffusion process related to the size of the Ln(III) ion or the difference in radii between the cations contained in the reactant oxides.

The most complete description of these systems will only be obtained from collating information and conclusions on the nature of the processes involved in all three systems, but a detailed discussion of individual systems is given below.

The La_2O_3-Cr_2O_3 system differs most significantly from the Nd_2O_3-Cr_2O_3 system, which is the only other system previously examined in a similar way, by forming in addition to the chromate (VI) compound the chromate (V) compound $LaCrO_4$. In all, the system produced three products, the two chromate compounds, and the only

thermally stable product, lanthanum chromite. The first question that must be resolved is the relationship of the reactions which form the chromate (V) and chromate (VI).

It has been shown that $LnCrO_4$ was formed as an unstable intermediate in the thermal decomposition of $Ln_2(CrO_4)_3$ by Schwarz (1963) and others, but no such mechanism is possible here. The most direct relationship between chromate (V) and chromate (VI) formation which could be postulated, assuming chromate (VI) is formed before chromate (V), is given in the equations below:-

$$La_2O_3 + Cr_2O_3 + O_2 \xrightarrow{(a)} La_2(CrO_4)_3 \xrightarrow{(b)} 2LaCrO_4 + \frac{1}{2}Cr_2O_3 + O_2$$

Such a facile scheme can be discounted since the isothermals in air, Figures 1-5, show that the rate of formation of chromate (V) at 560°C, 580°C, 600°C and 620°C is always greater than the rate of formation of lanthanum chromate (VI). In the process above if reaction (b) occurred at a rate always faster than reaction (a) then no chromate (VI) would form.

The reactions could be independent but parallel, i.e. occurring at the same time and in direct competition for the same reactants:-

$$La_2O_3 + Cr_2O_3 \xrightarrow{O_2} La_2(CrO_4)_3$$

$$La_2O_3 + Cr_2O_3 \xrightarrow[O_2]{} LaCrO_4$$

Although this can occur in homogeneous systems, for reactions in solids which must have a specific and localised site of reaction such

a process is just not possible. The variation of the amounts formed for each product at each temperature shows no constant relationship and this would also discount such a mechanism.

Further, there is no evidence to suggest that chromate (VI) can decompose at temperatures as low as those where chromate (V) is initially found. The reverse process of chromate (VI) forming from oxidation of chromate (V) is highly unlikely as chromate (VI) forms at a lower temperature than chromate (V); and, at temperatures around 600°C chromate (V) decreases to zero without affecting chromate (VI) formation.

Therefore it must be concluded that the formation of lanthanum chromate (V) and lanthanum chromate (VI) are completely independent, which explanation better fits the results. This statement must be qualified, however, for if two different reactions occur simultaneously on the same finite crystallite then there must ultimately be some competition for the same reactants. The morphology of the reaction is important in this connection and will be discussed at a later stage.

The formation of chromate (V) and chromate (VI) can now be treated as independent reactions. The same is true of their decompositions for there is excellent evidence that these are independent; for they do not occur in the same temperature range.

The reaction $2LaCrO_4 \rightarrow 2LaCrO_3 + O_2$ is considered below.

The graphs of the isothermals from 580-620°C immediately display a connection between the decrease of $LaCrO_4$ and the formation of $LaCrO_3$. Closer examination reveals that it is a precise relationship, likely to be quantitative, although this cannot be verified directly as the system is not static. It should be noted that the difference in weight between chromate (V) and the corresponding chromite is small and therefore the decomposition of 1% by weight $LaCrO_4$ would result in about 1% weight chromite. All the curves show the same process occurring, with the decrease in chromate (V) coinciding with the formation of chromite. Each graph shows the gradation in curve shapes and periods of decomposition expected of a rise in temperature. In the isothermal at 600°C, figure 4, the acceleratory period in decomposition of $LaCrO_4$ (4-7h.) coincides with the acceleratory period in chromite formation, and the deceleratory period of chromate (V) decomposition is during a period which is also deceleratory with respect to chromite formation (7-16h.). A graph of the combined product of chromite and chromate (V) against time at 590°C, figure 10, is smooth and continuous and shows the rate of formation of the products decreasing with time throughout.

The graphs of temperature dependence, figures 15 and 13, in oxygen for 8 hours, and for that in air at 32 hours clearly demonstrate the same relationship between chromate (V) decomposition and chromite formation. The temperature dependence in air was

carried out using the more reactive mixture and shows a rapid decrease of chromate (V) and increase in chromite between 560 and 600°C indicative of the reaction in the equation above. Similar behaviour is also shown in the temperature dependence in oxygen (less reactive mixture). In both cases, within experimental error, the graphs of combined chromate (V) and chromite products, figures 11 and 12, show a smooth curve deceleratory during the temperature range of transition, 620-670°C in oxygen and 560-600°C in air.

At these temperatures no decrease in lanthanum chromate (VI) is manifest and in any case the results indicate that in the formation of lanthanum chromite, the predominant mechanism is that of chromate (V) decomposition below 600-620°C in air at 32h. (more reactive mixture), and 660°C in oxygen, less reactive mixture. There is no suggestion that lanthanum chromate (VI) is involved below these temperatures; but, this is the predominant mechanism rather than the exclusive one, because the process is undoubtedly complex. Figure 8 shows the formation of lanthanum chromite from 580-640°C as a series of curves typical, in their sigmoidal shapes, of those obtained for isothermal decomposition of many solids, but here the increase in product is plotted, not the increase in partial pressure of a gas obtained in gaseous evolution from a decomposing reactant. This shape of curve can be explained by a mechanism involving nucleation, growth and overlap,

as noted earlier; but, the normal diffusion process responsible for the formation of lanthanum chromate (V) must continue, because the amount of total product exclusive of chromate (VI) formation continues to increase as shown in figure 10. This normal diffusion process will slow as the amount of product increases and is likely to be much slower than the growth step (acceleratory).of the decomposition process. Thus the sequence of diffusion is through:-

1) The 'normal' lanthanum chromate (V) lattice structure.
2) Various ratios of $LaCrO_4/LaCrO_3$ structures with slightly increased product layer.
3) The 'normal' $LaCrO_3$ structure, again with a slightly increased product layer.
4) A more perfect $LaCrO_3$ structure.

This order could explain why in the temperature dependence in air and oxygen, figures 13 and 15, the formation of chromite slows considerably, and according to the analysis results shows a slight decrease before rapidly increasing again. For the variation with temperature of the products in air, 560°C is a point of inflexion on a curve of the combined product of chromate (V) and chromite, figure 12; at this temperature a $LaCrO_3$ lattice rapidly begins to displace a lanthanum chromate (V) lattice. It may be, in part, that diffusion is easier through a $LaCrO_4$ lattice because of the intrinsic difference in structure.

During the decomposition of lanthanum chromate (V) to

chromite the rate of formation of chromate (VI) and its rate of increase with temperature were completely unaffected. Lanthanum chromate (VI) does not interfere with this process. This is in some ways a strange result since although the reactions are independent they do occur on the same crystallites.

The kinetic data shows the main difference between the behaviour of lanthanum chromates (VI) and (V) to be the rates of formation, extent of formation and kinetic stability. As shown by reactions in air, 350-700°C at 32h., chromate (VI) forms before chromate (V), but the rate of formation of chromate (VI) increases more slowly than that of chromate (V) with rise in temperature. Therefore diffusion must be more difficult, for it is unlikely to be a phase boundary process which is rate determining, because for chromate (VI), reaction begins at a lower temperature and this shows its initial ease of formation. The isothermals 560-640°C show that diffusion becomes difficult at each temperature after a definite but not fixed percentage of chromate (VI) has formed usually 12-15%. There is no comparable limit to lanthanum chromate (V) formation, save diffusion through a progressively thickening product layer, and therefore approaches a parabolic relationship. This difference can best be attributed, at this point in the discussion, to a physical constraint, imposed most probably, using the analogy of solid + gas reactions, by the surface of one reactant or other, assuming diffusion of the other reactant through the gas phase or along the surface. It

should not be considered that the limit at any temperature is representative of any multilayer formation, but rather, only consistent with the extent to which diffusion is possible at that temperature.

The decomposition of chromate (VI) is now considered as a preliminary survey of this topic, since many of the points raised will be discussed in depth later with evidence from the Pr_2O_3-Cr_2O_3 system.

The graphs of the temperature dependence in air and oxygen, figures 13 and 15, clearly show that the decrease of chromate (VI) is coincident with the further rapid formation of chromite, but the relationship between chromate (VI) decomposition and chromite formation is not precisely stoichiometric in the manner already shown for lanthanum chromate (V). From either temperature dependence results the amount of lanthanum chromate (VI) which manifestly decomposes could account for markedly less than half the amount of lanthanum chromite formed. It could be stated that the decomposition of chromate (VI) has a cooperative effect on chromite formation altering the rate of some other process in relation to its own decomposition. There is a theory of chromate (VI) formation and decomposition postulated by Gibb (1973) from results obtained in the Nd_2O_3-Cr_2O_3 system, and a critique of this will be produced when the results of the Pr_2O_3 system are considered with a view to finding a suitable explanation for chromate (VI) formation

and decomposition.

An explanation for the greater thermal stability of lanthanum chromate (VI) compared with chromate (V) and its slower decomposition may be obtained from a consideration of the peculiar structure of the chromate (VI) which is not known. Although it was stated that for the precipitated, dehydrated chromate (VI) that the structure might consist of chains of CrO_4 tetrahedra (Darrie, 1967), by analogy with $MgCrO_4$ and recently (Petrov et al., 1975) have from infra-red analysis deduced the structure of the precipitated hydrated chromate (VI) to be isolated CrO_4 tetrahedra. The results from infra-red spectroscopy of reacted samples obtained here also indicated the lack of anion-anion coupling in the structure of chromate (VI) prepared by solid state reaction. Isolated tetrahedra would radically alter the mechanism of nucleation and growth involved in decomposition, in comparison with a more coherent structure. It would effectively eliminate a cooperative process of decomposition as envisaged for $LaCrO_4$ and many other solids. This would greatly increase the number of nucleation processes required, assuming that an active nucleus could result from the decomposition of a single molecule; and as any growth stage would be extremely difficult each would only result in a small amount of chromite formation.

A temperature dependence study of the La_2O_3-Cr_2O_3 system under an argon atmosphere, between 600 and 975°C, where

no chromate formation was possible, showed that formation of lanthanum chromite occurred without chromate decomposition, as shown in figure 14. The amount of chromite formed at 600°C was 4% indicating that interaction was possible below this temperature, although reaction was fairly slow until 650°C. Thus in the absence of oxygen the interaction in this system is given by:-

$$La_2O_3 + Cr_2O_3 \rightarrow LaCrO_3.$$

The shape of the curve obtained here would suggest only the one mechanism for chromite formation and this from the results appears to be diffusion controlled. The amount formed rises steadily from 650-800°C and then slows considerably as the thickness of the product layer increases.

This does not indicate the nature of the diffusion process. In trying to reach an explanation for the temperature at which bulk diffusion processes begin the guidelines set out by Huttig (1936) are considered. The Tammann temperature, 0.52 x melting point °K of the solid, at which temperature lattice defects are considered to be mobile, and hence significant reaction begins, with concomitant bulk diffusion, is only a general guide and has some exceptions, one of which may be the systems studied here. The most characteristic reaction temperature, associated with the formation of chromite in all atmospheres, is 600°C. This is less than half the temperature of the melting point of the most volatile component Cr_2O_3. It may be then that the diffusion process is not bulk ionic diffusion via

defects; although, no great amount of stress should be placed on the non operation of a generalisation shown to have limited applicability. In argon, reaction is most likely to occur at the interfaces between the crystallites, with incipient product formation and subsequent diffusion being possible, as already shown, below or around 600°C.

This is of interest in connection with the formation of lanthanum chromate (V). There are three main questions to be asked in relation to the formation of chromate (V); why it forms, where it forms and how. At this point the where and the how might be discussed further.

The formation of lanthanum chromate (VI), it has been tentatively postulated, occurred on the surface to form a layer of product, diffusion occurring from the surface inward. This being the case, formation of lanthanum chromate (V) must occur elsewhere and be completely unaffected by chromate (VI) formation or decomposition and vice versa. The only part of the crystallite not directly exposed to the atmosphere is the interface, and, if reaction can occur here in the formation of chromite, this being the most straightforward procedure, then there is no reason why interfacial reaction should not take place in lanthanum chromate (V) formation. A link between chromate (V) and chromite formation in air has already been established in the 560-620°C temperature range. The shape of the curve of their combined products, figure

10, indicated that the fundamental diffusion process remained unaltered whether 100°/o chromate (V) was present or 100°/o chromite. A great disparity exists between the rate of formation of chromate (V) in oxygen and that of chromite in argon and an identical diffusion process can not reasonably be argued; but this could be explained by diffusion in an air or oxygen atmosphere being 'oxygen assisted' either with formation of chromium in a higher oxidation state or without this occurring. Further, if chromate (V) formation is initiated at the interface and chromate (VI) coats the surface it might be expected that the extent of formation of chromates (V) and (VI) would be affected by structure sensitive factors, e.g. the ratio of interface to resultant surface. The only major alteration of this type occurred in changing the Cr_2O_3 used, and this did indeed change the ratio of the amounts of chromate (VI) to chromate (V) formed.

Another feature of this system and no less significant in spite of the comparatively low yields, was the small amounts (1°/o), of chromite frequently detected in air or O_2 at low temperatures where no chromate (VI) or chromate (V) decomposition had occurred. This could possibly result from some initial interaction of the two reactant oxides without diffusion.

The effect of an increased partial pressure of oxygen in this system was studied by comparing air and oxygen atmospheres of 1 atmosphere with all other conditions kept constant over a range

of temperatures. The less reactive mixture was used and the results obtained were plotted in figure 16. The main findings are summarised below:-

1) At all temperatures the total product was greater in oxygen than in air.
2) The rate and the extent of formation of lanthanum chromate (V) were greater in O_2 than air.
3) Decomposition of chromate (V) began at a lower temperature in air than in O_2.
4) The initial rate of formation of chromite in air and oxygen were approximately equal.
5) The rate of formation and the amount of chromate (VI) formed was slightly greater in air than in oxygen.

In addition, the combined product of chromite and chromate (V) in oxygen always exceeded the yield in air from 580-640°C; also, the chromite formed in air exhibits only a slight increase in amount with rise in temperature from 620-640°C, thus indicating that diffusion had already become more difficult.

That lanthanum chromate (V) is much more sensitive than chromate (VI) to the increase in partial pressure of oxygen is in someways surprising, both processes require oxygen and chromate (VI) manifestly requires more than chromate (V). An explanation for this difference in sensitivity may be found in a comparison of the postulated mechanisms for chromate (V) and chromate (VI) formation.

The formation of lanthanum chromate (VI) involves two diffusion processes. The initial diffusion process is undoubtedly fast as shown by the formation of product at low temperature and initial rapid formation in the isothermals; while diffusion through the lanthanum chromate (VI) product layer essentially controls the rate of reaction. Oxygen may be involved in both diffusion processes, but primarily in the fast diffusion of one reactant to the surface of the other. Whereas reaction at the interface between the two oxides, as postulated for chromate (V) formation, requires the direct involvement of oxygen at the reaction centres, which the formation of chromate (VI) does not.

If the formation of chromate (V), as seems likely, is diffusion controlled then an increase in oxygen concentration greatly facilitates the diffusion process. It cannot, however, be stated with certainty whether diffusion through the lanthanum chromate (VI) product layer is assisted by oxygen because of the difference in competition from the chromate (VI) and chromate (V) forming reactions between air and oxygen.

The disparity in the amount of chromate (V) formed between air and oxygen could also explain why less chromate (VI) formed in oxygen than air.

The decomposition of chromate (V) occurs at a higher temperature in an oxygen atmosphere. A reason for this would have to explain the relative inhibition of the nucleation process of

chromate (V) decomposition in an oxygen atmosphere. It should also be noted that the amount of chromite formed is greater in air than in oxygen even before any decrease in chromate (V) has occurred in either atmosphere.

In view of the results obtained for this system the isothermal presented in the introduction as part of a survey of the work carried out by Rubinchik (1969) on the La_2O_3-Cr_2O_3 system can be re-examined. This isothermal shows typical behaviour of chromate (VI) in this system from 3-8 hours. However, it does not show typical behaviour in the period O-3 hours for the systems Ln_2O_3-Cr_2O_3, Ln = La, Pr or Nd shown here, or by Gibb (1973). The initial increase of the chromate (VI) is too great and the decrease too extensive at these reaction times. Further, the analysis used by Rubinchik would not distinguish between chromate (V) and (VI). It is likely that the curve is composite of these two products between O and 3h. reaction time, with the decomposition of the chromate (V) ensuring only the presence of chromate (VI) between 3 and 8h.

There are anomalies, exhibited in figure 9, showing total products v. time, where the amount of product does not increase with the rise in temperature. This can be attributed to slightly different mechanical and thermal pretreatments afforded to different mixtures. These small structure sensitive effects alter slightly the rate of diffusion at any temperature and time; but they are small

and can be ignored.

The differences between the behaviour of the Y_2O_3-Cr_2O_3 system and the La_2O_3-Cr_2O_3 system are considerable. The greatest difference is the very small amount of chromate formed in the yttrium system, where the nature of the chromate could not be identified, and this greatly limits the purview of the discussion. The following deductions can reasonably be made from results in the Y_2O_3-Cr_2O_3 system that,

1) The amount of chromate formed was greater in oxygen than in air,

2) Below 600°C the amount of chromate present in both air and oxygen was approximately constant,

3) Decomposition does take place around 600°C in both air and oxygen. There is also indirect evidence which suggests that the chromate is chromate (VI), based mainly on the reasonable assumption that lanthanum and yttrium chromates (V) would decompose at similar temperatures, about 600°C and then comparing this expected temperature with the greater thermal stability of the chromate formed here above 600°C. It is of interest to note that chromate is formed. Reaction must therefore have taken place between the reactants to form a product layer however thin and it is the subsequent inability of one reactant or other to diffuse through this layer which radically restricts the extent of reaction. If this is so then increased chromate formation in oxygen is likely to result from a slightly more efficient diffusion process rather than an

increased reaction at the phase boundary. It cannot reasonably be expected that the decomposition of this chromate, which begins around 600°C in oxygen and air, could effectively contribute to the production of chromite; but as shown experimentally the formation of chromite does respond to changes in the partial pressure of oxygen.

The amount of chromate decomposing is so small that even the promotion of some other mechanism, e.g. direct combination is not a reasonable supposition; neither would this explain the continued rate of increase of chromite formation in oxygen at higher temperatures where there is no chromate (VI) manifest. It is the effect of oxygen on this other mechanism which must be considered for an explanation of why the amount, and rate of formation of yttrium chromite is in the order oxygen > air >> argon. The mechanism can simply be presented as:-

$$Y_2O_3 + Cr_2O_3 \rightarrow YCrO_3.$$

The shapes of the temperature dependence curves are similar to those obtained for the lanthanum system in an argon atmosphere. This process is believed to be similar to that occurring during the formation of lanthanum chromite in argon involving formation of a product layer between the two reactants and diffusion of one reactant through the product layer thus enabling the reaction to proceed. The results show that here the increase in partial pressure of oxygen initiates chromite formation at a lower

temperature, in contrast to the lanthanum system; but in that system it was predominantly a decomposition mechanism which resulted in the production of chromite in the temperature range studied, and this as already stated, is not thought to be the mechanism involved in this case.

In the formation of chromite in argon no interaction with oxygen is possible and therefore a straightforward reaction between the phases could be imagined, either at the initial point of contact between the crystallites or possibly with preliminary gaseous or surface lattice diffusion to cover the other reactant, thus creating a larger interface and so facilitating the reaction; but the process must continue with diffusion through the product layer. The formation of chromite in air or oxygen is also likely to be a direct interfacial reaction. The chromate also formed in air and oxygen and believed to coat the surface is not responsible for the formation of the chromite. Diffusion through this small chromate layer, if possible to any extent would result in more chromate, not chromite. The formation of chromite is undoubtedly diffusion controlled. Thus an increase in oxygen concentration aids the diffusion process through the chromite product layer.

Before discussing the Pr_2O_3-Cr_2O_3 system it should be stated that the results obtained here are in many ways similar to the results for the corresponding neodymium system (Gibb, 1973); surprisingly so considering the differences in the nature of the

respective lanthanide (III) oxides, but this very difference has provided more information concerning the central questions of chromate and chromite formation than might otherwise have been achieved. The difference between this and other lanthanide (III) oxide-chromic oxide systems resides in the oxidation of the praseodymium (III) oxide.

It has been shown, in either an atmosphere of air or oxygen, that the oxide reaches a limit given by the formula PrO_x, $x = 1.833$, (Pr_6O_{11}) for the extent of oxidation. Although this degree of oxidation is not attained instantaneously it does occur very quickly at the temperatures of reaction, e.g. at 600°C after 1 min. $x = 1.779$. Thus the starting mixture is effectively $PrO_{1.779}$-Cr_2O_3 before reaction between the oxides commences.

The formation of $Pr_2(CrO_4)_3$ is now considered. One feature of chromate (VI) formation which is again exhibited is the formation of appreciable quantities at fairly low temperatures. The temperature dependence plot in air, figure 19, indicates that significant amounts are formed at 480°C. Another feature is the initially rapid formation of praseodymium chromate (VI) as shown in the isothermal at 600°C, figure 28, where about 5% product was obtained after 15 minutes. Both these trends would be typical of a relatively fast diffusion process, almost temperature independent, as indicated by the temperature dependence plots, where the decrease in the amount of chromate (VI) formed below 480°C is likely to be

small.

It was noted above that the crystallites of Pr_2O_3 were oxidised extremely quickly, ultimately to Pr_6O_{11}, in air, but during isothermal reaction or from the variation of product with temperature the state of oxidation represented by the formula Pr_6O_{11} is never obtained. It can also be seen that initially the oxidation state of the praseodymium oxide decreases during reaction as the chromate (VI) increases, but although nearly all reactions analysed contained at least 4°/o chromate (VI) extrapolation of the Pr(III) or Pr(IV) content to zero time, e.g. in the isothermal at 600°C, figure 34, indicates that the extent of oxidation, x = 1.833 consisting of 37.78°/o Pr(IV) and 19.46°/o Pr(III) was never reached. The extent of oxidation attained by extrapolation would in fact be not much greater than the value given by x = 1.779 obtained after 1 minute oxidation at this temperature.

The conclusion to be drawn from this evidence is that the oxide is prevented by exclusion of oxygen from its surface from being further oxidised to its experimentally determined limit. Thus a very rapid diffusion of a chromium containing species must have very quickly covered the surface, probably in about 1 min. at 600°C and there react to form praseodymium chromate (VI), possibly at a slower rate. Conceivably reaction would be expected to proceed through diffusion of the chromium containing species through the product layer to the oxide interface and this would no doubt be rate determining.

The experiment of Savchenko (1973) in which he observed a coating of chromate (VI) on a Nd_2O_3 pellet placed approximately 1mm away from a Cr_2O_3 pellet, showed that gas phase diffusion of a surface oxidised Cr_2O_3 species was feasible, and the possibility of gas phase diffusion of CrO_3 or an oxidised chromium species has often been proposed. It had been used by Hulbert et al. (1968) to explain reaction in the $MgO-Cr_2O_3$ system, and by analogy with this system, by Gibb (1973) to account for formation of neodymium chromate (VI). There seems little doubt that such a process could account for the initial rapid diffusion of chromium to the surface of the praseodymium oxide crystallite; but diffusion of molecules along the surface cannot be excluded.

One of the surprising results to emerge from the investigation of this system is that the chromium-oxygen species only appears to react with the Pr(IV) component of the unreacted oxide. It has been shown in the absence of appreciable amounts of chromite that the trend of decrease in the Pr(IV) component of the unreacted praseodymium oxide and increase of the Pr(III) of the oxide and that of the praseodymium in the chromate (VI) is a general one. The trend above is also consistent as demonstrated in the results section. The decrease in praseodymium (IV) is equal within experimental error to the sum of the increase in the Pr(III) component of the oxide and the praseodymium within the chromate (VI) at every temperature and time; although the ratio of the amounts

of praseodymium chromate (VI) to Pr_2O_3 (oxide) formed is not constant. This variation does not make it possible to write a balanced equation but the process can be represented by:-

$$[PrO_2]_{oxide} + Cr_2O_3 \xrightarrow{O_2} Pr_2(CrO_4)_3 + [Pr_2O_3]_{oxide}$$

As given above the only cause of Pr(IV) reduction could be the chromium species. Thus it is likely that at the point of interaction with Pr(IV) it was in an oxidation state less than VI. The reaction to form praseodymium chromate (VI) must be highly complex involving interaction of $[PrO_2]$, chromic oxide and oxygen. The oxygen is probably not 'free' but associated with the chromium and the diffusion process since free oxygen would probably re-oxidise. $[Pr_2O_3]_{oxide}$. The formation of praseodymium chromate (VI) can be represented by the series of processes below:-

1) $Cr_2O_3.\text{surface} + O_2 \rightarrow Cr_2O_3.(O_2)$ diffusable species

2) $Cr_2O_3.(O_2) - O_2 \rightarrow Cr_2O_3.\text{surface}$

3) $Pr_2O_3 + O_2 \rightarrow [PrO_2.Pr_2O_3]$ oxide

4) PrO_2 oxide $+ Cr_2O_3 + O_2 \rightarrow Pr_2(CrO_4)_3 + Pr_2O_3$ oxide

5) $Cr_2O_3 \xrightarrow[\text{diffusion through product layer}]{O_2} Cr_2O_3(PrO_x \text{ interface})$

(Thereafter reaction continues as in 4)

The diffusion process through the product layer will slow as the thickness of the layer increases and this is shown in the graphs of the isothermals, figure 36, as the decrease in rate of formation of the chromate (VI) with time. Although the deceleratory nature of the reaction is marked, it is much less so than that observed for the

formation of lanthanum chromate (VI). The plots of chromate (VI) in the praseodymium system show similar characteristics to curves whose reactions followed a logarithmic law in contrast to the limiting one observed for lanthanum chromate (VI) and the apparent parabolic law of lanthanum chromate (V) formation. The rate of diffusion through the product layer will increase with rise in temperature and this is also shown in figure 36, which shows the variation with time of chromate (VI) at each temperature. There are two opposing factors: initially the thickness of the product layer will increase with rise in temperature but this will more effectively hinder any further transport process from occurring; thus it might be expected that at higher temperatures the subsequent product formation would the sooner show deceleratory effects. This also is observed. This graph also shows the decrease in chromate (VI). The decrease in chromate (VI) and the formation of praseodymium chromite is now reviewed.

It is easy to see a connection between chromate (VI) decomposition and increase in chromite, from figures 24-28 , 19 and 21, but it is not immediately obvious what relationship exists between these two. It is not, however, identical to that shown for lanthanum chromate (V) decomposition and lanthanum chromite formation. An explanation for the formation of chromite was postulated by Gibb (1973) from work on the Nd_2O_3-Cr_2O_3 system. Its main weakness was the assumption that below 1000°C, chromate

decomposition was the only mechanism available for the formation of chromite, based on the experimental evidence of 3 reactions undertaken in argon, where chromate formation was impossible, which showed no formation of chromite; although chromite can be formed without chromate decomposition as shown for many Ln_2O_3-Cr_2O_3 systems including all those studied here. This absence of chromite in these three reactions, however, led to the argument that the rate of formation of neodymium chromate (VI) and its rate of decomposition were very precisely linked in order to account for the quantities of chromite formed.

Consider figures 19 and 21 showing the temperature dependence for 8 hours reaction, in air and oxygen respectively. Below 600°C in air no formation of chromite has occurred and at 620°C in oxygen very little chromite has formed. There has been no significant decomposition of chromate (VI) for there are no decomposition products in air below 600°C and very little decomposition below 620°C in oxygen assuming that here all the chromite resulted from chromate decomposition. Now assuming that above these temperatures all the chromite was a result of chromate decomposition, then it is easy to work out how much chromite a given amount of chromate (VI) decomposition would produce. Above 600°C in oxygen the increase in the amount of chromite would require an extremely large increase with rise in temperature of chromate (VI) formation, where previously the amount of chromate (VI)

had been decreasing with rise in temperature. This increase in chromate (VI) formation would not be observed; this to explain the experimental evidence which shows no increase, because of a concomitant and slightly greater decomposition of the chromate (VI) with rise in temperature such that the resultant amount of chromate was just below the amount it had been at a slightly lower temperature. This is patently and completely untenable: it is not a dynamic system. A similar analysis of the isothermal at 600°C, figure 28, gives the same conclusion. Between O and 8h. the formation of praseodymium chromate (VI) is slowing, there is no significant decomposition to account for the decrease and manifestly the decrease continues between 8 and 16h. The increase in chromite between 8 and 16h. if attributed to the decomposition of chromate (VI) would require the rate of formation of chromate (VI) from 8-16h. to increase with time during this interval, but also for the rate of decomposition of the chromate (VI) to occur at a rate just slightly less than the rate of formation. The result being, that only a small increase in the amount of formation was observed between 8 and 16h. in accord with the deceleratory nature of the formation of chromate (VI) below 8h. This is an extremely unlikely hypothesis and must be rejected.

Therefore chromite formation cannot be explained in terms of chromate decomposition alone either in air or oxgyen. It has already been stated in connection with the formation of chromate (VI) that a specificity of reaction of Cr_2O_3 with $[PrO_2]$

oxide had been established in its production. The statement can be made that here the Pr(III) component of the unreacted oxide is not involved directly in the formation of chromate (VI), and this indeed increases slightly as the chromate (VI) is formed.

The formation of significant amounts of chromite begins before the maximum of chromate (VI) has been achieved and this increase in chromite coincides more precisely with the decrease in the Pr(III) oxide component which always apparently preceeds the manifest decomposition of praseodymium chromate (VI). Thus another process in the formation of praseodymium chromite is the reaction of the Pr(III) component of the oxide with chromic oxide:-

$$Pr_2O_3.\text{oxide} + Cr_2O_3 \rightarrow PrCrO_3.$$

It had previously been stated, perhaps too categorically, that the formation of chromate (VI) was not a dynamic process; by this it was not meant that as decomposition began formation ceased: rather that the rate of formation during decomposition should be consistent with the trend in the rate of formation before decomposition, which in nearly every case was very slow. Thus to clarify the nature of the formation of chromite and the extent of the engagement of the different processes the following illustrations are considered

i) Isothermal at 600°C in air

ii) Temperature dependence in air 600-680°C.

i) Isothermal at 600°C in air (figure 34)

a) In the period 8-16h.

Increase in $PrCrO_3$ = 8.09% ≡ 4.64% Praseodymium

Increase in $Pr_2(CrO_4)_3$ = 3.03% ≡ 1.32% praseodymium

Decrease in Pr(IV) oxide = 3.92%

Decrease in Pr(III) oxide = 2.16%

Total increase = 5.96% and the total decrease = 6.08%; therefore within experimental error they are consistent.

The major problem in the interpretation of these results is the inability to say with complete certainty how the decrease in Pr(IV) is divided between the increase in Pr(III) and the praseodymium in the chromate (VI) according to the equation:-

$$[PrO_2] \text{ oxide} + Cr_2O_3 \xrightarrow{O_2} Pr_2(CrO_4)_3 + [Pr_2O_3] \text{ oxide},$$

since chromite is now being formed, but it is possible to make reasonable assumptions based on trends in the previous periods. A comparison is made of the decrease in Pr(IV) and the respective increases in Pr(III) in periods where chromite is absent, and present. Thus an indication of how Pr(IV) is likely to proportion between the praseodymium in chromate (VI) and the Pr(III) component of the oxide is obtained. Although here the majority of chromite formed as the result of direct combination, it seems likely that some decomposition of chromate (VI) had occurred, since a decrease of 3.92% in Pr(IV) would be expected to produce more chromate (VI) than is actually observed, based on a comparison of the experimental results of the previous period.

The process can be represented as:-

$$PrO_2 + Cr_2O_3 \rightarrow Pr_2(CrO_4)_3 + Pr_2O_3$$

$$Pr_2O_3 + Cr_2O_3 \rightarrow PrCrO_3$$

$$Pr_2(CrO_4)_3 \rightarrow 2PrCrO_3 + \tfrac{1}{2}Cr_2O_3$$

b) In the period 16-32h.

In this period the Pr(IV) content of the oxide is approximately constant then;

Increase in praseodymium chromite = 27.33°/o

Decrease in Pr(III) component of the oxide = 11.70°/o ≡ 20.00°/o $PrCrO_3$

Decrease in praseodymium chromate (VI) = 9.60°/o ≡ 7.34°/o $PrCrO_3$

Total = 27.34°/o $PrCrO_3$

Here all the chromite formed in this period can be accounted by the reactions below:-

1) $Pr_2O_3 + Cr_2O_3 \rightarrow PrCrO_3$

2) $Pr_2(CrO_4)_3 \rightarrow 2PrCrO_3 + \tfrac{1}{2}Cr_2O_3$

It appears that the majority of the chromite formed always occurs by direct combination as in 1) above.

ii) Temperature dependence in air 600-680°C, figure 19

From 600-680°C praseodymium chromite increases by 46.00°/o.

From 600-680°C, decrease in Pr(III) = 16.50°/o ≡ formation of 28.12°/o $PrCrO_3$

From 620-680°C, decrease in chromate (VI) = 12.00°/o ≡ formation of 9.2°/o $PrCrO_3$

From 600-620°C, decrease in praseodymium chromate (VI) = 1.5°/o ≡ 0.34°/o praseodymium content of the chromate (VI)

From 600-620°C, decrease in Pr(IV) oxide = 5°/o praseodymium.

Thus (5-0.34)°/o Pr(IV) oxide would produce 8°/o $PrCrO_3$.

Thus the total chromite produced from these various sources is (28.21 + 9.2 + 8.00)°/o = 45.21°/o, and this accounts for the observed increase in chromite formation from 600-680°C.

Therefore chromite formation is a complex process consisting of two main mechanisms, which do not, however, appear to be completely independent. The temperature dependence characteristics of Pr(III) decrease and chromate (VI) decomposition are almost identical in oxygen, as evident in figure 22, and similar in air as shown by figure 20.

A correlation between the decrease of Pr(III) and $Pr_2(CrO_4)_3$ is also indicated, although less clearly, in the isothermals. This is shown by comparison of figures 36 and 39 and inspection of figures 30-34. Thus it would appear that the rates of these two processes are alike.

Further, a comparison of the temperature dependence in air and oxygen, shows that both Pr(III) and the chromate (VI) begin to decrease at a higher temperature in oxygen than in air. There is no apparent reason why this should be, if there were no connection between the two processes. Therefore these two processes are most probably concerted.

In argon the system is once more greatly simplified, no chromate formation is possible nor is oxidation of praseodymium (III)

oxide, figure 23. Again the formation of 5°/o chromite at 600°C, a higher yield than in air or oxygen at this temperature and time, signifies diffusion below 600°C. The amount of chromite increases steadily as from 600°C diffusion through the product layer continues and then gradually slows as the product layer thickens; although, almost 50°/o reaction had occurred before this became marked. Again the reaction can only be represented by the equation:-

$$Pr_2O_3 + Cr_2O_3 \rightarrow PrCrO_3.$$

It is of course possible to postulate various mechanisms for diffusion, but there seems to be no reason why initial reaction should not occur interfacially, proceeding with bulk diffusion. This is the most straightforward mechanism and the one favoured as an explanation of the results.

The most characteristic differences between the reactions in air and oxygen, see figures 19-22, have already been described in the results section. Again the effects of increase in partial pressure of oxygen are complex, but one of the two most significant features is the increase in the amount of chromate (VI) formation in oxygen. The Pr(IV) component of the praseodymium oxide was shown to be involved in the formation of praseodymium chromate (VI), but in either air or oxygen at 1 atmosphere the extent of oxidation of the praseodymium oxide was invariable. This cannot then explain the increased formation of $Pr_2(CrO_4)_3$ in an oxygen atmosphere, and therefore the praseodymium oxide must play essentially a passive

role. The other important feature is the smaller amounts of chromite formed in oxygen between 600 and 640°C with greater amounts formed above this temperature.

It has been stated that the amount of chromate (VI) formed was controlled by the rate of diffusion through the product layer. Therefore increased O_2 partial pressure increases the rate of diffusion through this layer. The formation of chromite occurs at a higher temperature in oxygen, as did formation of chromite and decomposition of chromate (V) in the La_2O_3-Cr_2O_3 system; but it was seen that where an entirely direct combination process was postulated for the Y_2O_3-Cr_2O_3 system that increasing the partial pressure of oxygen increased the amount of chromite formed and lowered the temperature of its initial formation. This would suggest that in the Pr_2O_3-Cr_2O_3 system, the decomposition of chromate (VI) controls the direct combination process in the concerted mechanism postulated. This is in apparent contradiction to the observation that Pr(III) decrease occurs at a lower temperature and at shorter reaction times than praseodymium chromate (VI), but small amounts of chromate (VI) may decompose before the observed maxima, and an analysis of the figures in i) a) shows that this is possible.

None of this explains why in oxygen, the rate of decomposition of chromate (VI) is faster, and the direct combination process proportionately so; or why, for either, the product layer presents a less effective barrier to diffusion than it did in air. The

system must be complex with oxygen playing an important and dynamic, but ill defined role. It was possible to calculate the amount of chromite formed by 'direct combination' in air and oxygen by attributing this to the observed decrease in the Pr(III) component of the unreacted oxide. A comparison of these calculated amounts of chromite with the amount formed in argon over a comparable temperature range 600-720°C resulted in this order:-

Argon < Air < Oxygen.

The Pr_2O_3-O_2 system is also extremely complex. As shown, in an atmosphere of air or oxygen the formula can with reasonable accuracy be represented as Pr_6O_{11}, but during reaction in the Pr_2O_3-Cr_2O_3 system the mean oxidation state of the praseodymium oxide varies. In has been shown (Guth and Eyring, 1954) that the structure of the oxide varies almost continuously with its mean oxidation state. Thus a series of polymorphic transitions would be taking place. If Hedvall's observation of increased reactivity during such transformations were applicable here, abnormally high reaction rates because of these changes, might be expected. There is nothing that suggests abnormally high reactivity in this system in relation to other Ln_2O_3-Cr_2O_3 systems already studied. In the systems Ln_2O_3-Cr_2O_3 Ln = La, Nd or Y, there are no polymorphic transformations possible at reaction temperatures (Roth and Schneider, 1960). Therefore, neither could the Hedvall effect explain the increased reactivity in these systems always

associated with temperatures around 600°C.

Praseodymium chromate (V) was also formed in this system, but only in the isothermal at 560°C and there its behaviour was in certain ways anomalous to that for chromate (V) in the La_2O_3-Cr_2O_3 system, see figures 29 and 35. As in the lanthanum system the chromate (V) formed here would only appear to be stable at temperatures below 600°C and for relatively shorter reaction times, but as seen in figure 35 the decrease in chromate (V) from 4 to 8h. did not result in a concomitant increase in chromite. There does, however, appear to be a connection between the unexpected decrease in $[Pr_2O_3]_{oxide}$ and chromate(V) formation. This would give a chemical explanation for the difference in formation of chromate (V) and chromate (VI) different from the fundamentally morphological one postulated for lanthanum chromate (V) formation. Thus it would also appear that the reaction:-

$Pr_2O_3 + Cr_2O_3 \xrightarrow{O_2} 2PrCrO_4$ was reversible, but too much should not be inferred from one series of results.

The final part of the discussion is an attempt to collate material and to try and establish criteria for the reactivity in the Ln_2O_3-Cr_2O_3 systems. Considerations of a decrease in general reactivity across the lanthanide series or more correctly with decreasing size of the lanthanide cation failed to reach a concrete explanation; although this reactivity series was believed to be related to a structure insensitive diffusion process. Particularly,

the decrease in reactivity between the praseodymium and neodymium systems does not appear to be associated with any change in the nature of the processes involved, from a comparison taken over a wide range of temperatures and times which show very similar kinetics. There is also some reason to believe that reactivity in the yttrium system is a limiting case of this decrease in reactivity with special relevance to chromate (VI) formation. Whereas the formation of lanthanum chromate (V), and some praseodymium chromate (V) does indicate a difference in the nature of these systems to others studied.

The two most important questions to emerge are 1) Can the mechanism of chromate (VI) formation/decomposition as developed for the praseodymium system be applied in general to all the systems Ln_2O_3-Cr_2O_3, and 2) Why is chromate (V) formation so very important in the lanthanum system, and yet not as significant for the praseodymium system and not at all for the neodymium system.

This latter question is not easy to answer. The reason for the difference must be more specific than that which could be attributed to some general decrease in reactivity connected with ionic radii, although this may be a contributary factor. If not directly related to the size of the lanthanide ion then what other properties chemical or physical of the ions would allow the formation of chromate (V) for these two systems, and also produce such a disparity between them. The electronic configuration of the ion and the

resultant energy states of the solid seems a possibility, but not one which is plausible on close scrutiny. There is no relationship which would account for the observed product formation in these systems.

Another approach is to examine the properties of the chromates (V) formed or not formed. Lanthanum chromate (V) is different from other lanthanide chromate (V) compounds in its possession of the Huttonite structure, while praseodymium chromate (V) appears to be unique in having a mixture of the Huttonite and Zircon structures. The possibility arises that $LnCrO_4$ does not form in other systems because the geometry of the reaction, most probably of the diffusion process, is not appropriate for the production of the Zircon structure but is for the formation of the Huttonite structure.

The characteristics of chromate (VI) formation in the systems Ln_2O_3-Cr_2O_3, Ln = La, Pr, Nd are in a number of ways very similar. Lanthanum of this three is slightly different because the rate of formation approaches more nearly a limiting law than the other two. This can be explained by the formation of the chromate (V) restricting chromate (VI) formation and thus accentuating the effects of progressively slower diffusion, which situation does not apply in other systems. It would seem likely that a similar mechanism can be applied to all three systems because the kinetics are similar, but it was shown that in the praseodymium system that Pr(IV) played a part in chromate (VI) formation, whereas there is no stable La(IV)

or Nd(IV) ion formed in their respective systems. If the mechanisms were identical the formation of La(IV) or Nd(IV) ions would have to be postulated, and although it is possible that under the conditions of reaction that Nd(IV) could possibly form and play some role in the mechanism this is not possible for lanthanum, where Ln(IV) is unknown. It may be that the formation of an Ln(IV) ion is not essential to the formation of $Ln_2(CrO_4)_3$. It is not the only oxidising species even in the Pr_2O_3-Cr_2O_3 system and the role played by oxygen, together with Cr_2O_3, may be of paramount importance and thus may lead to formation of chromate (VI) without the formation of an Ln(IV) ion. The presence of Pr(IV) in the praseodymium system does not appear to be the determining factor in the formation of chromate (VI), as shown by the results of the temperature dependence in an oxygen atmosphere. Thus it may be that a basically similar mechanism of chromate (VI) formation exists for all Ln_2O_3-Cr_2O_3 systems studied.

A similar arguement to that adopted in discussing chromate (VI) decomposition in the Pr_2O_3-Cr_2O_3 system could if applied to the corresponding lanthanum system, have produced similar reasons why chromate decomposition alone was not responsible for chromate formation and would have introduced the possibility of a direct combination process $La_2O_3 + Cr_2O_3 \rightarrow LaCrO_3$ to account for the difference.

There is thus no difficulty in attributing chromite formation

in the lanthanum system above 680°C, 8h, O_2 (less reactive mixture) and 620°C, 32h., air (more reactive mixture) figures 15 and 13 repsectively, to the same processes which occur in the Pr_2O_3-Cr_2O_3 system.

Several aspects of the reactivity in these systems have been discussed in terms of, or attributed to, a diffusion process, which appears to have seminal importance for some of the reactions in the Ln_2O_3-Cr_2O_3 systems, Ln = La, Pr, Y. Given below is a compilation of features believed to be associated with the diffusion mechanism, aside from the reasonably well known effects produced by an increase in temperature or an increase in thickness of the product layer.

1) Apart from an initial gas phase or surface diffusion of a chromium-oxygen species in the formation of chromate (VI); it is primarily a bulk diffusion process which is important.

2) Bulk diffusion is assisted by increasing the oxygen concentration.

3) The Ln(III) ion, although static and therefore probably associated with the crystal structure of the newly formed product, affects the facility of diffusion. The ease of diffusion increases as the size of the Ln(III) ion increases.

4) The diffusing cation is Cr^{3+}.

5) The crystal structure of a possible product determines to a large extent whether diffusion will proceed with formation of that product e.g. $LaCrO_4$ forms but $NdCrO_4$ does not form.

REFERENCES

Andreeva, A.B. and Keler, E.K.; Zh. Prikl. Khim 39(3) 489 (1966).

Bertaut, F., Buisson, G. and Mareschal, J.; Compt. Rend., 259 411 (1964).

Brauer, G. and Pfeiffer, B.; J. Less Common Metals, 5 171 (1963).

Britton, H.T.S.; J.Chem. Soc., 125 1875 (1925).

Campbell, L.J.; University of Edinburgh, unpublished results (1975).

Cassedanne, J.O.; An. Acad. Brasil. Cienc., 40(1) 57 (1968).

Clifford, A.F.; Proc. Conf. Rare Earth Res. (3rd), (1963); Publ. 1964.

Cohn, G.; Chem. Rev. 42 527 (1948).

Darrie, R.G.; Ph.D. Thesis, University of Edinburgh (1967).

Darrie, R.G., Doyle, W.P., and Kirkpatrick, I.; J. Inorg. Nucl. Chem. 29(1) 979 (1967).

Duval, T. and Duval, C.; Anal. Chim. Acta, 2 218 (1948).

Eckschlager, K.; "Errors, Measurements and Results in Chemical Analysis", Publ. Van Nostrand, London (1969).

Eyring, L.; "Rare Earth Research", Ed. J.F. Nachman and C.E. Lundin, Publ. Gordon and Breach, New York, p. 339 (1962).

Figgis, B.N. and Lewis, J.; 'Modern Coordination Chemistry', Ed. Lewis J. and Wilkins, R.G., Interscience (1960).

Galwey, A.K.; 'Chemistry of Solids', Chapman and Hall (1967).

Gibb, G.; Ph.D. Thesis, University of Edinburgh (1973).

Guth, E.D. and Eyring, L.; J. Am. Chem. Soc. 76 5242 (1954).

Hulbert, S.F., Brosnan, D.A. and Smoak, R.H.; Proc. 6th Int. Symp., Reactivity of Solids (1968).

Huttig, G.F.; Angew. Chem. 49 882 (1936).

Kirkpatrick, I.; Unpublished results, University of Edinburgh (1966).

Koehler, E.K., Leonov, A.I., Shvaiko-Shvaikovskii, V.E.; Therm. Anal. Proc. Int. Conf. (3rd) (1971), Publ. 1972.

Leonov, A.I., Andreeva, A.B., Shvaiko-Shvaikovskii, V.E. and Keler, E.K.; Izv. Akad. Nauk SSSR, Neorgan Materialy 2(3) 517 (1966).

Looby, K.T. and Katz, L.; J. Am. Chem. Soc. 76 6029 (1954).

Lopato, L.M., Yaremenbo, Z.A. and Shevchenko, A.V.; Izv. Akad. Nauk SSSR, Neorgan Materialy 6(6) 1055 (1966).

Pavlikov, V.N., Lopato, L.M. and Tresvyatskii; Izv. Akad. Nauk SSSR, Neorgan Materialy 2(7) 1244 (1966).

Pavlikov, V.N., Lopato, L.M. and Tresvyatskii, S.G.; Izv. Akad. Nauk SSSR, Neorgan Materialy 2(4) 679 (1966).

Pavlikov, V.N. and Tresvyatskii, S.G.; Zh. Neorgan Khim. 11 (6) 1442 (1966).

Pavlikov, V.N. and Tresvyatskii, S.G.; Vopr. Teorii i Primeneniya Red kozem. Metal., Akad. Nauk SSSR, p.159 (1964).

Perel'man, F.H. and Fedoseeva, E.I.; Zh. Neorgan Khim. 8 (11) 2603 (1963).

Petrov, K.I., Voronskaya, G.N., Bashilova, N.I. Takhanova, E.S.; Zh. Neorg. Khim. 20 (1) 72 (1975).

Portnoi, K.I., Timofeeva, N.I., Fadeeva, V.I.; Zh. Neorgan Khim. 10 (9) 2041 (1965).

Portnoi, K.I. and Timofeeva, N.I.; Izv. Akad. Nauk SSSR, Neorgan Materialy 1 (9) 1593 (1965).

Prokudina, S.A., Rubinchik, Ya,S. and Pavlyuchenko, M.M.; Izv. Akad. Nauk SSSR, Neorg. Mater. 8 (2) 293 (1972).

Pryde, I.J.; Ph.D. Thesis, University of Edinburgh (1971).

Quezel-Ambrunaz, S. and Mareschal, M.; Bull. Soc. Franc. Mineral Cryst., 86 (2) 204 (1963).

Roth, R.S. and Schneider, S.J.; J. Res. Natl. Bur. Std. 64A 309 (1960).

Rubinchik, Ya, S., Banekovskaja, S.K. Kniga, M.V. and Mochalnick, I.A.; Vesti Akad. Navuk Belaruss. S.S.R., Khim. Novak 6 86 (1972).

Rubinchik, Ya. S., Mochalnik, I.A. and Pavlyuchenko, M.M.; Izv. Akad. Nauk. S.S.S.R. Neorg. Mater. 8 (1) 133 (1972).

Rubinchik, Ya. S., Pavlyuchenko, M.M. and Mochalnik, I.A.; Vesti. AN Belaruss. S.S.R., Khim. Navuk 2 23 (1969).

Rubinchik, Ya.S., Prokudina, S.A. and Pavlyuchenko, M.M.; Vesti. Akad. Navuk. Belaruss. S.S.R., Ser. Khim. Navuk, (3) 17 (1972).

Rubinchik, Ya. S., Veremei. T.P., Pavlyuchenko, M.M. and Mochalnik. I.A.; Dokl. Akad. Nauk. Beloruss. S.S.R. 17 (9) 830 (1973).

Ruggiero, A. and Ferro, R.; Gazz. Chim. Ital. 85 892 (1955).

Savchenko, V.F. and Rubinchik, Ya.S.; Vesti. Akad. Navuk, Beloruss. S.S.R., Khim. Novak (3) 75 (1973).

Savchenko, V.F., Rubinchik, Ya.S. and Pavlyuchenko M.M.; Vesti. Akad. Navuk. Beloruss. S.S.R., Ser. Khim. Novak. (5) 87 (1973).

Schneider, S.J., Roth, R.S. and Waring, J.L.; J. Res. Natl. Bur. Std. 65 A 345 (1961).

Schwarz, H.; Z. Anorg. Allgem. Chem. 322 1 and 129 (1963).

Sevost'yana, N.I., Murav'eva, I.A., Kovba, L.M., Martynenko, L.I. and Spitsyn, V.I.; Dokl. Akad. Nauk. S.S.S.R. 161 (6) 1359 (1965).

Shevchenko, A.V., Lopato, L.M., Pavlikov, V.N.; Izv. Akad. Nauk S.S.S.R., Neorg. Mater. 5 (12) 2128 (1969).

Shevchenko, A.V., Lopato, L.M. and Yaremenko, Z.A.; Dopov. Akad. Nauk. ukr. S.S.R. Ser. B 29 (10) 925 (1967).

Stone, F.S., Tilley, R.J.D.; Proceedings of the 7th Symposium on the Reactivity of Solids (1972).

Vogel, A.I.; Inorganic Quantitative Analysis, Longmans (1954).

Welch, A.J.E.; 'Chemistry of the Solid State', Ed. Garner, W.E., Publ. Butterworths (1955).

Wold, A. and Ward, R.; J. Am. Chem. Soc. 76 1029 (1954).

Zambanini F and Carrobbi, G.; Rend. Accad. Sci. Napoli 31 17 (1925).

APPENDICES

1) Polymorphism of the lanthanide oxides

Table I - La_2O_3

Table II - Pr_2O_3

Table III - Y_2O_3

2) Visible and Ultra-Violet Spectra

Table IV - $La_2(CrO_4)_3$

Table V - $LaCrO_4$

Table VI - $LaCrO_3$

Table VII - Cr_2O_3

3) Infra-red Spectra

Table VIII - $La_2(CrO_4)_3 . 7H_2O$

Table IX - $La_2(CrO_4)_3$

Table X - $LaCrO_4$

Table XI - $LaCrO_3$

Table XII - Cr_2O_3

4) X-ray powder diffraction (d-spacings Å)

Table XIII - $La_2(CrO_4)_3 . 7H_2O$

Table XIV - $La_2(CrO_4)_3$

Table XV - $LaCrO_4$

Table XVI - $LaCrO_3$

Table XVII - Cr_2O_3

1) Polymorphism of the lanthanide oxides

Table I - La_2O_3 (d-spacings Å)

La_2O_3, calcined 900°C, 4h	A-type La_2O_3 (Literature)
3.40 (29)	3.41 (34)
3.055 (32)	3.063 (31)
2.969 (100)	2.980 (100)
2.270 (27)	2.278 (58)
1.965 (34)	1.968 (63)

Literature :- Swanson and Fuyat NBS Circular 539, Vol. III (1953)

Table II - Pr_2O_3 (d-spacings Å)

Pr_2O_3 (reduced from Pr_6O_{11})	A-type Pr_2O_3 (Literature)
3.34 (41)	3.34 (35)
3.225 (84)	
3.01 (33)	3.01 (40)
2.922 (100)	2.92 (100)
2.784 (33)	
2.233 (20)	2.24 (35)
1.969 (38)	
1.929 (39)	1.929 (40)

Literature :- Div. Applied Phys., Polytechnic Inst. Brooklyn, N.Y.

(1955)

Table III - Y_2O_3 (d-spacings Å)

Y_2O_3 calcined 900°C, 4h	C-type Y_2O_3 (Literature)
4.31 (15)	4.32 (15)
3.005 (100)	3.01 (100)
2.652 (32)	2.648 (28)
2.502 (6)	2.495 (6)
2.260 (9)	2.254 (7)
2.076 (10)	2.076 (11)
1.868 (52)	1.870 (49)

Literature :- Swanson and Fuyat, NBS, Circular No. 539, Vol. III (1953).

2) Visible and Ultra-Violet Spectra

Table IV - $La_2(CrO_4)_3$

Measured (nm)	Literature (nm)
410, peak	375, peak
275, shoulder	280, peak

Literature :- Darrie (1967).

Table V - $LaCrO_4$

Measured (nm)	Literature (nm)
785, peak	780, peak
650, peak	650, peak
395, peak	400, peak
300, shoulder	300, shoulder

Literature :- Darrie (1967).

Table VI - $LaCrO_3$

Measured (nm)	Literature (nm)
	685, peak
	655, peak
615, peak	615, peak
480, peak	465, peak
370, peak	365, peak
345, peak	325, peak

Literature :- Darrie (1967).

Table VII - Cr_2O_3

Measured (nm)	Literature (nm)
603, peak	600, peak
503, shoulder	
470, peak	475, peak
340, peak	380, peak

Literature :- Gibb (1973).

3) Infra-red Spectra

Table VIII - $La_2(CrO_4)_3.7H_2O$

Measured (cm^{-1})	Literature (cm^{-1})
1640, m	1640, s, sh
1595, w	
945, s	945, w
918, s	915, s
890, s	895, s
860, s. sp	860, m
843, s. sp	840, w
820, s. sp	820, m
620, m	630, m.sh
434, w	432, m
395, w	
380, w	

Literature :- Darrie (1967)

Table IX - $La_2(CrO_4)_3$

*Measured (cm^{-1})	Literature (cm^{-1})
1002 m, sp.	
980 m, sp.	
935 vs.	930 w, sp.
920 s, sp.	920 s.
904 s, sp.	900 w, sp.
860 s, sp.	
826 vs., sp.	
803 vs.	
	790 s.
	775 s.
458 w	
440 w	
386 vw.	
373 vw.	
348 vw.	

Literature :- Darrie (1967)

* sintered 550°C (1h)

Table X - $LaCrO_4$

Measured (cm^{-1})	Literature (cm^{-1})
845, s	845, w
812, m	810, m
725, s	734, s
421, m	
373, w	
355, m	

Literature :- Darrie (1967)

Table XI - $LaCrO_3$

Measured (cm^{-1})	Literature (cm^{-1})
630, vs.	640, s
580, vs.	580, s
	(continues below 500 cm^{-1})
418, s	
382, m	
355, w	
330, w	

Literature :- Darrie (1967).

Table XII - Cr_2O_3

Measured (cm^{-1})	Literature (cm^{-1})
	685, sh
625, s	625, s
570, s	570, s
540, sh	530, sh
446, m	442, m
418, m	415, m
308, w	

Literature :- Gibb (1973).

4) X-ray powder diffraction (d-spacings Å)

Table XIII - $La_2(CrO_4)_3 \cdot 7H_2O$

Measured (Å)	Literature (Å)
8.98 (100)	9.21 (100)
6.40 (11)	
5.30 (21)	5.37 (17)
4.73 (17)	4.67 (20)
4.58 (19)	
4.25 (26)	4.29 (15)
3.97 (11)	3.99 (9)
3.80 (11)	3.81 (7)
3.59 (12)	3.63 (5)
3.44 (14)	3.48 (5)
3.25 (32)	3.25 (19)
3.19 (39)	3.21 (26)
3.10 (26)	
3.06 (17)	
3.02 (21)	
2.863 (11)	2.876 (9)
2.849 (11)	
2.730 (11)	2.746 (10)
	2.698 (10)
	2.667 (15)
2.652 (16)	2.652 (17)
2.481 (11)	

Literature :- Darrie (1967)

Table XIV - $La_2(CrO_4)_3$

Measured (Å)	Literature (Å)
	10.65 (20)
	9.60 (20)
6.53 (51)	6.56 (90)
5.44 (43)	5.44 (80)
4.59 (36)	
4.57 (36)	
3.77 (26)	
3.74 (30)	
3.72 (30)	
3.63 (40)	3.65 (50)
3.58 (57)	3.57 (50)
3.48 (21)	
3.09 (100)	3.09 (100)
2.931 (26)	
2.899 (51)	2.894 (30)
2.858 (13)	
2.841 (15)	
2.512 (38)	
2.191 (26)	
2.161 (26)	

Literature :- Darrie (1967)

Table XV - $LaCrO_4$

Measured (Å)	Literature (Å)
5.37 (11)	
4.77 (13)	
4.32 (21)	4.33 (15)
	4.15 (20)
3.60(26)	3.59 (20)
3.37 (63)	3.39 (80)
3.19 (100)	3.18 (100)
3.06 (18)	3.07 (18)
2.936 (80)	2.95 (82)
2.706 (24)	2.714 (25)
2.535 (22)	2.535 (24)
2.254 (15)	
2.215 (18)	2.217 (18)
2.176 (9)	2.176 (19)
	2.041 (20)
2.004 (34)	2.002 (40)
1.933 (24)	1.937 (30)
1.914 (10)	1.918 (24)
1.832 (13)	1.830 (24)

Literature :- Darrie (1967)

Table XVI - $LaCrO_3$

Measured (Å)	Literature (Å)
3.85 (21)	3.85 (18)
2.730 (100)	2.730 (100)
2.230 (19)	2.233 (18)
1.935 (38)	1.933 (34)
1.731 (8)	1.728 (9)

Literature :- Darrie (1967)

Table XVII - Cr_2O_3

Measured (Å)
3.59 (67)
2.644 (97)
2.458 (100)
2.161 (43)

ABSTRACT OF THESIS

Name of Candidate BRIAN CORMACK

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Degree Ph.D. *Date* 9/10/75

Title of Thesis SOLID-STATE REACTION BETWEEN TWO OXIDES

Reactions between solid oxides were studied for the systems Ln_2O_3-Cr_2O_3; Ln = La, Pr and Y, by following the variation of products with temperature or time, at temperatures below 1000°C, employing predominantly chemical analysis.

In the La_2O_3-Cr_2O_3 system three products formed in an atmosphere of air or oxygen, $LaCrO_4$, $La_2(CrO_4)_3$ and $LaCrO_3$. The chromate (V) compound decomposes to chromite at temperatures around 600°C, whereas the chromate (VI) compound decomposes at slightly higher temperatures. In argon only $LaCrO_3$ formed. The way in which the two chromates are formed, and decompose to chromite was delineated and a mechanism was advanced in explanation.

The only significant product in the Y_2O_3-Cr_2O_3 system, $YCrO_3$, formed in varying extent in different atmospheres in the order argon<air<oxygen. The experimental evidence was related to a mechanism for chromite formation.

The Pr_2O_3-Cr_2O_3 system was complicated, by the oxidation of the Pr_2O_3 oxide, in air or oxygen atmospheres. The variation in the oxidation state of the oxide was followed analytically during the reaction, thus affording a more precise investigation of the nature of its interaction with chromic oxide. A mechanism for chromate (VI) formation and decomposition to the chromite, was propounded. In this system $PrCrO_4$ formed in an isothermal at 560°C.

Use other side if necessary.